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SERIES II.—Time, $2\frac{1}{2}$ hours. Temperature, 130—140°.

NO_2 : Cl.	Acid formed.	Calculated as chloro-nitrotoluene.	M. p. of acid. Found.	M. p. of acid. Correct.	Unchanged substance.	Total.
2 : 3	0·103	0·088	185—200°	235°	0·869	0·957
3 : 2	0·530	0·451	177—181	179	0·460	0·911
2 : 4	0·542	0·461	124—136	140—143	0·383	0·844
4 : 2	0·583	0·496	135—140	142—144	0·486	0·982
2 : 5	0·316	0·269	123—134	137—138	0·646	0·915
5 : 2	0·436	0·371	157—161	165	0·565	0·936
2 : 6	0·327	0·278	145—155	161	0·639	0·917
3 : 4	0·672	0·572	170—177	178—180	0·279	0·851
4 : 3	0·634	0·540	136—141	185—186	0·403	0·943
3 : 5	0·432	0·368	146—149	148—149	0·584	0·952

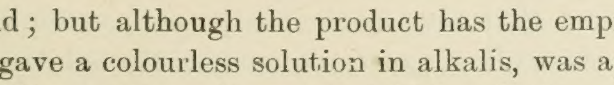
THE UNIVERSITY,
LEEDS.

XCIII.—*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide. Part I.*

By ARTHUR LAPWORTH and ELKAN WECHSLER.

IN extending the investigation of cyclic β-cyanoketones (Trans., 1906, **89**, 955, 1819, and 1869) a method of degrading these to open-chain compounds was sought for and cyanodihydrocarvone was the first compound experimented on, as it is comparatively easy to obtain in considerable quantity. The method of breaking open the ring by the Beckmann process applied to the oxime, or Baeyer's method in which Caro's reagent is used to oxidise the ketone, failed to give satisfactory results. The use of alkyl nitrites in presence of mineral acids, which with saturated ketones containing the group $:CH\cdot CO\cdot$ often causes ring scission, was in this instance avoided because of the probability of attack at the propenyl group. Conversion of the compound into an α-monocarboxylic ester or the α-cyano-derivative was attempted, but again without success.

The effect of amyl nitrite in presence of sodium ethoxide instead of mineral acids was next investigated, it being anticipated that the *iso*nitroso-compound,

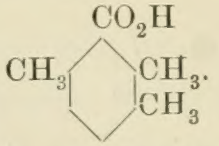


$$CH_3\cdot CH<\begin{matrix}CH(CN)\cdot CH_2\\ CO—C(:NOH)\end{matrix}>CH\cdot C<\begin{matrix}CH_3\\ CH_2\end{matrix},$$

would be found; but although the product has the empirical formula $C_{11}H_{14}O_2N_2$ it gave a colourless solution in alkalis, was apparently not affected by boiling with sodium bisulphite solution, and was not decomposed like *iso*nitrosocamphor when heated in glacial acetic acid with sodium nitrite. After treatment with boiling acetyl chloride it was nearly all recovered unchanged and, although it reacted with phosphorus pentachloride in the cold, the product when poured into water once more yielded the original substance.

It did not respond to any of the usual tests for ketonic compounds, and when heated with alkalis in presence of ferrous hydroxide did not yield a trace of ferrocyanide, the absence of the group $:C(CN)\cdot \underset{\bullet}{C}H\cdot CO\cdot$ thus being indicated.

When the compound was warmed for some days with hydrochloric acid on the water-bath, ammonium chloride and a crystalline acid were formed, carbon dioxide being eliminated. The new acid had the formula $C_9H_{11}\cdot CO_2H$, was optically inactive, and when distilled with soda-lime gave a large proportion of a benzenoid hydrocarbon which was identified as ψ-cumene, of which, therefore, the inactive acid was evidently a nucleal monocarboxylic acid; as it was not identical with the two known nucleal acids it follows that it was probably the third, namely, that having the structure



The mechanism of the curious change whereby this compound was produced from cyanodihydrocarvone appeared worthy of careful investigation, and experiments have been in progress during the last two years with the object of ascertaining, if possible, what are the intermediate stages in this conversion, involving also the atttempt to establish the constitution of the compounds dealt with. This paper contains an account of some of the more important results hitherto obtained.

The action of cold acids on the supposed *iso*nitroso-compound was first investigated. This leads to the formation of (*a*) an isomeric compound (L′),* $C_{11}H_{14}O_2N_2$, with properties very like those of the original material, and probably stereoisomeric with it, (*b*) of two isomeric basic substances B and B′, $C_{11}H_{16}O_3N_2$, formed by union with one molecular proportion of water. The relative amounts of these three products depends on the concentration of the mineral acid and the duration of its action.

When the original compound or the base formed in largest quantity is warmed with excess of sodium hydroxide for some time, traces of ammonia are evolved, and on subsequent titration of the solutions with acids it is found that one molecular proportion of alkali has been neutralised. On adding excess of acid to the solution in the latter instance the base is recovered unchanged, so that lactone formation occurs almost instantaneously.

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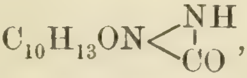
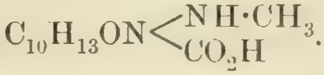
* For convenience in referring to some of the compounds dealt with, they are designated by suitable letters or symbols. The supposed *iso*nitroso-compound having proved to be a lactam is referred to as the lactam (L).

In the case where the original compound (L) has been treated with excess of alkali, addition of mineral acid causes the precipitation of a new carboxylic acid (A) having the formula $C_{10}H_{15}ON_2{\cdot}CO_2H$. This is amphoteric in character, dissolves readily in sodium carbonate solution and also in concentrated hydrochloric acid, and in the latter instance a crystalline hydrochloride is sometimes obtained. It is reconverted into the compound (L) by heat or by treatment with certain dehydrating agents, which suggests that the acid (A) contains an amino-group as well as a carboxyl group and may be represented as

$$C_{10}H_{13}ON{<}\begin{matrix}NH_2\\CO_2H\end{matrix},$$

and that the compound (L) is its lactam,  $C_{10}H_{13}ON{<}\begin{matrix}NH\\|\\CO\end{matrix}$, a view supported by the bitter taste associated with the latter substance.

Satisfactory confirmation of this supposition has been obtained by converting the sodium derivative of the lactam into its methyl derivative (LMe) by the action of methyl iodide. This has no longer any acidic character, a fact explained by the conversion of the group ${\cdot}NH{\cdot}CO{\cdot}$ into ${\cdot}N(CH_3){\cdot}CO{\cdot}$, but it is converted on heating with alkalis into the methylated amino-acid (AMe),  $C_{10}H_{13}ON{<}\begin{matrix}NH{\cdot}CH_3\\CO_2H\end{matrix}$. Both the methylated lactam and the acid are converted by cold strong hydrochloric acid into a basic compound closely resembling the lactonic base (B) of which it represents the methyl derivative and may be referred to as (BMe).

When the methylated base (BMe) is warmed with dilute acids and the solution is subsequently rendered alkaline and distilled, methylamine is evolved in nearly quantitative amount, an observation which supplies the last link in the chain of evidence that the supposed *iso*nitrosocyanodihydrocarvone (L) is a lactam which owes its acidic character to the presence of the ${\cdot}NH{\cdot}CO{\cdot}$ group.

The principal product besides methylamine, which results on hydrolysis of the base (BMe) with dilute acid, is identical with that which is obtained, together with ammonia, by the similar treatment of the non-methylated base (B). It is an acid which has the formula $C_{11}H_{17}O_5N$ and will be referred to as "the lactonic acid." It may be titrated with sodium hydroxide and behaves as a monobasic acid, but when warmed with excess of alkalis for some time it neutralises two equivalent proportions. Like the bases (B) and (BMe) therefore, it is lactonic in character, and the original acid is regenerated when liberated from the solution of the disodium salt.

Although the lactonic acid behaves in the cold as a monobasic acid and decomposes carbonates, there is reason to doubt if it is a carboxylic acid, for if it is dissolved in ice-cold potassium carbonate and treated with potassium permanganate a compound separates from the alkaline solution which contains certainly either 10 or 11 carbon atoms, as shown by the ratio between the content of carbon and nitrogen, and yet no carbon dioxide, formic acid, or any other compound which could conceivably be produced by the elimination of one or two carbon atoms appears to be formed at the same time. We are forced to conclude therefore that the oxidation product contains all the carbon atoms present in the original compound, which therefore can hardly be a carboxylic acid. The lactone ring which it contains is thus probably the same as that present in the base (B) and arises from the carboxylic group of the amino-acid (A).

This acid gives a series of characteristic colour reactions and when it is heated with dilute mineral acids it is slowly transformed into trimethylbenzoic acid, with evolution of carbon dioxide and ammonia. It is extremely stable towards hot alkalis, apart from the rupture of the lactone ring, but it is reduced if ferrous hydroxide is present, ammonia being liberated. The products of this change are at present under examination.

The absence of a colour reaction with ferric chloride in the case of the base suggests that the change whereby it yields the lactonic acid involves the replacement of $\cdot\mathrm{NH}_2$ by $\cdot\mathrm{OH}$, the latter having a phenolic function. If so, then the grouping $>\mathrm{C}{:}\dot{\mathrm{C}}\cdot\mathrm{NH}_2$ is present in the base (B) and in the acid (A) from which it is obtained. This is perhaps the cause of the peculiar behaviour of the last two compounds towards nitrous acid; both yield yellow precipitates with nitrous acid in extremely dilute solutions, but the methylated compounds do not behave in this way, nor does the lactonic acid from which the amino-group has been removed. It seems not unlikely that the formation of these products depends on the intermediate existence of diazo-compounds which the presence of the grouping $>\mathrm{C}{:}\dot{\mathrm{C}}\cdot\mathrm{NH}_2$ would probably facilitate, since aromatic amines contain this otherwise unusual complex. The comparatively low basicity of these derivatives and the acid reaction of the amino-acids, a class of substances usually nearly neutral towards indicators, is perhaps also attributable to this structure.

The discussion of the precise constitution of the compounds described in this paper as well as of their relationship to the original cyanodihydrocarvone may be deferred until further experimental evidence has been adduced.

EXPERIMENTAL.

The Lactam (I), $C_{10}H_{13}ON<\genfrac{}{}{0pt}{}{NH}{CO}$.

$C_{10}H_{13}ON<\genfrac{}{}{0pt}{}{NH}{|\atop CO}$

Dihydrocyanocarvone (59 grams) was mixed with an ice-cold solution of sodium (8 grams) in absolute alcohol (200 c.c.) and amyl nitrite (43 grams) gradually added, the temperature not being allowed to rise above 0°. The whole was allowed to remain for about twelve hours, when it was poured into about ten times its bulk of water. After filtering from a small quantity of resinous matter, carbon dioxide was passed into the clear brown solution, and the new compound separated as a white, voluminous, gelatinous precipitate; this was collected, dried, and crystallised from alcohol. The yield was about 45 grams:

0·2434 gave 0·5734 CO_2 and 0·1495 H_2O. C = 64·2; H = 6·9.

0·1282 ,, 14·35 c.c. moist nitrogen at 11° and 773 mm. N = 13·6.

$C_{11}H_{14}O_2N_2$ requires C = 64·0. H = 6·8; N = 13·4 per cent.

The substance is very readily soluble in alcohol, chloroform, acetone, benzene, acetic acid, or ethyl acetate, less readily so in ether, carbon tetrachloride or carbon disulphide, sparingly soluble in cold carbon disulphide and nearly insoluble in light petroleum. It dissolves to some extent in hot water and the solution has a very bitter taste. It crystallises from alcohol or from hot water in slender needles melting at 138—139°.

The crystals are flat and show straight extinction in polarised light, their directions of greatest length and elasticity being coincident. When fused between glass slips the compound sets to translucent patches which crack radially from a number of centres, whilst at the edges of the mass are seen a few large, flat needles or oblique, six-sided plates.

One gram, dissolved and made up to 25 c.c. with absolute alcohol, was examined in a 2-dcm. tube at 15°. The observed rotation was +9·68°, whence $[\alpha]_D$ +121°.

The substance dissolves in a solution of sodium hydroxide, forming a colourless solution from which it is precipitated by carbon dioxide or sodium hydrogen carbonate as a mass of minute needles. It at once discharges the colour of ice-cold potassium permanganate or that of a solution of bromine in acetic acid, even when sodium acetate is present.

As this compound was at first believed to be an ordinary *iso*nitroso-derivative of cyanodihydrocarvone, many attempts were made to cause it to undergo the Beckmann transformation. It was recovered unaltered, however, after prolonged treatment with boiling acetyl chloride, cold phosphorus, pentachloride, or trichloride, or with toluenesulphonic chloride and hot sodium hydroxide or pyridine. With hot phosphorus chlorides it was attacked, but the products contained much phosphorus. No trace of hydrogen cyanide was removed on boiling the substance with sodium hydroxide and ferrous hydroxide, but ammonia was liberated. It was not altered when heated with sulphurous acid in acetic acid solution or with boiling sodium bisulphite, and when shaken in sodium hydroxide solution and benzoyl chloride no benzoyl derivative was formed.

The Isomeric Lactam (L′), $C_{11}H_{14}O_2N_2$.

The lactam (*L*) dissolves in a cold saturated aqueous solution of hydrogen bromide with evolution of heat. Ten grams were dissolved in 30 c.c. of the acid, any considerable rise of temperature being avoided. The solution was allowed to stand for thirty minutes and was then poured into water. A very voluminous, white precipitate separated, which was collected, washed with water, and crystallised first from alcohol and then from benzene. Yield, 3·5 grams:

0·2935 gave 0·6942 CO_2 and 0·1738 H_2O. C = 64·50; H = 6·58.
0·1576 ,, 13·74 c.c. moist nitrogen at 10° and 763·4 mm. N = 13·74.
$C_{11}H_{14}O_2N_2$ requires C = 64·08; H = 6·79; N = 13·59 per cent.

The substance resembles the isomeric compound in general behaviour towards solvents, and separates from alcohol or benzene as a colourless, crystalline powder. On heating, it begins to turn yellow at about 160°, and melts completely to a red liquid at 180°.

It dissolves in cold sodium hydroxide solution, forming a colourless liquid from which it is reprecipitated unaltered by carbon dioxide, and generally resembles the isomeric lactam in chemical character.

The Amino-acid (A), $C_{10}H_{13}ON<\substack{NH_2\\CO_2H}$.

A solution of 20 grams of the lactam (L) in a 10 per cent. aqueous solution of sodium hydroxide (160 c.c.) was heated on the water-bath for five hours. The cooled solution was acidified with dilute hydrochloric acid and the precipitate collected, washed, and crystallised from boiling water or dilute alcohol. The yield of purified acid was 20 grams:

0·3152 gave 0·7582 CO_2 and 0·2280 H_2O. C = 58·9; H = 7·2.
0·2342 ,, 25·6 c.c. moist nitrogen at 21° and 760·5 mm. N = 12·5.
$C_{11}H_{16}O_3N_2$ requires C = 58·9; H = 7·1; N = 12·5 per cent.

0·8085 required 3·6 c.c. *N*-sodium hydroxide for neutralisation, whence the equivalent 225; the number calculated for a monobasic acid, $C_{11}H_{16}O_3N_2$, being 224.

The substance is sparingly soluble in boiling water, but dissolves freely in alcohol, glacial acetic acid, or acetone, and is nearly insoluble in ether, chloroform, benzene, or light petroleum. It separates from alcohol in short, colourless prisms, and from hot water in feathery aggregates of colourless needles melting at 155°.

The crystals, when small, are truncated, deeply striated needles having straight extinction in polarised light. In other cases, short, transparent prisms or rectangular prisms may be obtained. Crushed fragments of the larger crystals occasionally show in convergent polarised light one axis of a wide-angled, interference figure. The double refraction is moderate.

After fusion between glass slips, the compound solidifies slowly, and only when hot, to masses of long, curved, fibrous, parallel needles, the whole being much cracked in directions parallel to the needles.

0·8892 Gram dissolved and made up to 25·1 c.c. with absolute alcohol was examined in a 2-dcm. tube at 13°. The observed rotation was $-2·92°$, whence $[\alpha]_D$ $-41·2°$.

The substance reacts strongly acid to litmus and expels carbon dioxide from solutions of carbonates. A neutral solution of the sodium salt gives with silver nitrate a white precipitate which is soluble in ammonia or in boiling water, being slowly decomposed in the latter instance, with deposition of metallic silver. With ferric chloride a pale red, and with mercuric chloride a white, precipitate is formed; no precipitates are obtained with soluble calcium, barium, or lead salts.

The acid is amphoteric in character, and dissolves appreciably more freely in dilute mineral acids than in water. When covered with concentrated hydrochloric acid, colourless crystals, probably of a hydrochloride, are formed, but these are decomposed on addition of water. No sparingly soluble platinichloride or aurichloride could be obtained, but an oily periodide is precipitated even from very dilute solutions of the acid on addition of hydriodic acid containing iodine in solution. The salts do not reduce boiling Fehling's solution, nor is the latter affected by the product obtained on heating the acid for some time with dilute mineral acids, so that hydroxylamine is not formed in the latter instance although ammonia may be detected. A solution of the acid in ten times its weight of 10 per cent. aqueous sodium hydroxide was heated on the water-bath for seven hours, but on acidification yielded the original acid almost entirely unchanged, and no appreciable quantity of ammonia was evolved.

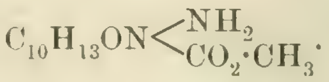
Neutral solutions of the salts instantly decolorise dilute ice-cold permanganate solution and the free acid at once discharges the colour of a solution of bromine in acetic acid, alone or with excess of sodium acetate. It is also attacked by alkaline hypobromite, but no bromoform is produced.

The acid is very easily oxidised or reduced. When warmed with lead peroxide in dilute acetic acid solution, it is rapidly attacked and carbon dioxide is evolved, but profound decomposition occurs. It is not easily reduced by zinc with ammonia, acetic acid, or sodium hydroxide, or by sodium amalgam, but with sodium and alcohol it yields oily amino-acids. It is rapidly reduced in the cold by tin and hydrochloric acid, or by ferrous hydroxide and alkali, ammonia being formed. When it was heated with sodium bisulphite solution, a yellow coloration was developed, ammonia was found in the solution, and a stable organic sulphonic acid appeared to have been formed. The products obtained in some of these reactions have not yet been isolated in a pure form and are at present under examination.

Attempts to prepare a benzoyl derivative of the acid by treating it with benzoyl chloride in warm pyridine or by the Schotten-Baumann reaction were unsuccessful, the acid being recovered unaltered, although in both instances the benzoyl chloride is decomposed very rapidly, the acid apparently acting as a catalyst. With toluenesulphonic chloride and alkali, a gummy acid containing sulphur was obtained in small quantity.

When the acid is shaken with benzaldehyde and dilute aqueous sodium hydroxide the aldehyde dissolves rapidly, but is apparently only oxidised catalytically. On heating it with aqueous phenylhydrazine acetate on the water-bath, ammonia is evolved and a red neutral oil separates; at the ordinary temperature no change occurs. With hydroxylamine the acid is converted into an oil which is sparingly soluble in water and contains combined hydroxylamine, as it does not reduce Fehling's solution at once, but does so after being heated with dilute acids.

Methyl Ester of the Amino-acid (A), $C_{10}H_{13}ON<\begin{matrix}NH_2\\CO_2\cdot CH_3\end{matrix}$.



This substance may be obtained either by shaking the cooled alkaline solution of the acid in a considerable excess of 10 per cent. sodium hydroxide with a slight excess of dimethyl sulphate or by heating the silver salt of the acid with methyl iodide dissolved in absolute methyl alcohol. In the former case the product separated as an oil which crystallised when immersed in a freezing mixture; in the latter instance the crude product was purified by shaking it with dilute, aqueous sodium carbonate.

The compound is readily soluble in most of the usual media with the exception of cold water and light petroleum, and crystallises from dilute alcohol in thin, fragile, rectangular plates which have straight extinction in polarised light and melt at 99—100°.

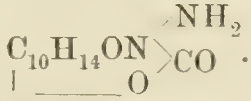
This ester is very distinctly basic in character, dissolves readily in dilute acids, forming colourless solutions from which it is reprecipitated by alkalis. It is insoluble in cold sodium hydroxide, but when heated with that reagent it dissolves slowly and the solution, on acidification, yields the derived amino-acid (A).

Conversion of the Amino-acid (A) *into the Lactam* (L).

When the amino-acid (A) was heated under reduced pressure it decomposed and water and some ammonia were evolved. The residue was extracted with aqueous sodium hydroxide and the filtered solution saturated with carbon dioxide, when a white mass was precipitated, which crystallised from alcohol in white needles melting at 139°, and was identical with the lactam (L).

The lactam may also be obtained from the amino-acid by boiling it for about nine hours with glacial acetic acid, or by treating it with excess of acetic anhydride or phosphorus trichloride. In these cases secondary reactions occur; the yield of the lactam is nearly quantitative, however, when acetyl chloride is used as a dehydrating agent.

The Lactonic Base (B),



$$\underbrace{C_{10}H_{14}ON\begin{matrix}\nearrow NH_2\\ \searrow CO\end{matrix}}_{O}.$$

The lactam (L) dissolves in cold concentrated hydrochloric acid without evolution of heat. If the solution is immediately diluted, the lactam is precipitated unchanged. If, however, the solution is allowed to stand for several days a few colourless needles, the hydrochloride of a base, separate. The main product of the reaction remains in the solution, and is precipitated on neutralising it with alkali. It is basic in character, but differs from the base obtained from the crystals.

Ten grams of the lactam (L) were dissolved in 50 c.c. of concentrated hydrochloric acid, and allowed to stand for two days. The solution was then neutralised with sodium hydroxide and the precipitated base collected and purified by crystallisation from hot water. The yield of crystallised product was 9·2 grams:

0·2151 gave 0·4634 CO_2 and 0·1397 H_2O. C = 58·75; H = 7·22.
0·1756 ,, 18·3 c.c. moist nitrogen at 10° and 765 mm. N = 12·6.
$C_{11}H_{16}O_3N_2$ requires C = 58·88; H = 7·14; N = 12·5 per cent.

The compound dissolves in hot water, from which it separates almost completely on cooling in stellar aggregates of long, colourless needles. It is readily soluble in alcohol, chloroform, glacial acetic acid, or acetone, but only slightly so in benzene or ether. It melts at 122—123°.

The large crystals of the compound are transparent prisms, faintly, but thickly, striated with longitudinal lines. The smaller ones are needles in which the directions of greatest elasticity and length are at right angles. Crushed fragments examined in convergent, polarised light show a uniaxial figure. The double refraction is strong and negative in sign. When fused it solidifies very slowly and incompletely, even at a temperature a few degrees below its melting point.

For the determination of the optical activity, 0·9985 was dissolved and made up to 24·9 c.c. with absolute alcohol, and examined in a 2-dcm. tube at 13°. The rotation observed was +0·525°, whence $[\alpha]_D$ +6·55°.

It is distinctly basic in character, dissolving readily in dilute acids, and forming crystalline salts. It decolorises bromine instantly, even in the presence of sodium acetate, and is also immediately oxidised by an ice-cold solution of potassium permanganate. It is very stable towards alkalis; after heating a solution in ten times its weight of 10 per cent. sodium hydroxide for thirty hours on the water-bath, the greater part was recovered unchanged on acidification, but when warmed with a measured quantity of $N/10$ sodium hydroxide for a few minutes and the alkali titrated with $N/10$ acid, it was found that salt formation had occurred.

0·2036 after boiling with 24·5 c.c. $N/10$ NaOH required 15·4 c.c. $N/10$ H_2SO_4, whence the equivalent = 224; the number calculated for a monobasic acid, $C_{11}H_{16}O_3N_2$, is 224.

The base is evidently the anhydro-derivative of a monocarboxylic acid, and is probably a lactone.

It is rapidly decomposed on heating with sodium hydroxide and ferrous hydroxide, ammonia being evolved in considerable quantity. A very dilute solution of the base in acids instantly gives a lemon-yellow precipitate on addition of sodium nitrite.

With acetyl chloride a vigorous reaction occurred, and an oily substance was formed, which was decomposed by warm dilute sodium carbonate solution, the original base being regenerated. Probably an unstable, acetyl derivative had been produced. It did not yield a semicarbazone, an oxime, or a phenylhydrazone.

The *hydrochloride*, $C_{11}H_{16}O_3N_2$,HCl, was prepared by adding hydrochloric acid to an alcoholic solution of the base (B) and precipitating with ether. It was obtained as a white mass of small needles:

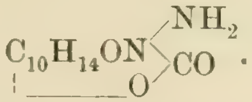
0·7765 gave 0·4313 AgCl. Cl = 13·7.

$C_{11}H_{16}O_3N_2$,HCl requires Cl = 13·6 per cent.

Direct Conversion of the Amino-acid (A) *into the Lactonic Base* (B).

On mixing the amino-acid with five times its weight of cold concentrated hydrochloric acid the mass at first set to a solid cake, probably of the hydrochloride as already suggested, but when this was stirred a clear liquid was finally obtained. At the end of twenty-four hours, on neutralising the solution with sodium hydroxide, a white compound was precipitated which crystallised from water in colourless needles melting at 122—123°, and was in all respects identical with the lactonic base (B). The yield was about 60 per cent. of the calculated amount.

Isomeric Base (B′),



$$\underset{\vert\_\_\_\_\_\_\_\_\_O}{C_{10}H_{14}ON}\left\langle\begin{matrix}NH_2\\CO\end{matrix}\right. .$$

The crystals which separated from the solution of the lactam (L) in hydrochloric acid yielded on decomposition with alkali a base which was crystallised from hot water :

0·3165 gave 0·6823 CO_2 and 0·2044 H_2O. $C = 58·79$; $H = 7·17$.

0·1736 ,, 18·85 c.c. moist nitrogen at 18·5° and 764 mm. $N = 12·57$.

$C_{11}H_{16}O_3N_2$ requires $C = 58·88$; $H = 7·14$; $N = 12·50$ per cent.

This base is therefore isomeric with the one previously described. It is formed in small quantity by the action of hydrochloric acid on the lactam (L′), but can be obtained in an almost quantitative yield by treating the isomeric lactam (L′) with hydrochloric acid. It is readily soluble in hot alcohol, glacial acetic acid, or acetone, very sparingly soluble in cold alcohol, chloroform, benzene, or ether, and insoluble in light petroleum. It is fairly soluble in hot water, from which it separates almost completely on cooling in colourless crystals melting at 157—158°.

The crystals are opaque, fern-like forms, and the compound after fusion sets slowly and incompletely to a mass of small, thin plates with strong, double refraction ; the optical characters of these forms could not be distinguished.

0·290 Gram dissolved and made up to 20 c.c. with absolute alcohol was examined in a 2-dcm. tube at 15°. The observed rotation was + 0·18, whence $[\alpha]_D + 6·21°$.

Action of Nitrous Acid on the Lactonic Base

On adding a solution of sodium nitrite to a dil
base in hydrochloric acid, a lemon-yellow, amo
separated in light, flocculent masses practical
All attempts to purify the substance by cr

solvents were unsuccessful, and it was therefore merely washed with water and dried on porous porcelain in a vacuum:

0·1991 gave 0·4076 CO_2 and 0·1231 H_2O. C = 55·83; H = 6·75.
0·1009 „ 10·575 c.c. moist nitrogen at 14° and 757·5 mm. N = 12·3.
$C_{21}H_{32}O_7N_4$ requires C = 55·75; H = 7·08; N = 12·38 per cent.

The reaction takes place according to the equation:

$$2C_{11}H_{16}O_3N_2 + HNO_2 + H_2O = C_{21}H_{32}O_7N_4 + CO_2 + NH_3.$$

That this equation does actually express the course of the reaction was confirmed by titrating a solution of the base in dilute sulphuric acid with sodium nitrite solution until the filtered liquid gave no further precipitate with the reagent. It was thus found that 2 molecules of the base required 1·03 molecules of sodium nitrite for complete precipitation; the filtrate was free from nitrous acid, but contained ammonia.

The substance dissolves readily in alcohol, ether, benzene, glacial acetic acid, or chloroform to yellow solutions, from which it separates in the form of a resin; it is not dissolved by light petroleum. On heating, it begins to soften at 75°, and decomposes with evolution of gas at about 98°. It dissolves in sodium hydroxide to a deep yellow solution, from which it is reprecipitated on addition of acids; it also dissolves, but not so readily, in aqueous sodium carbonate. Its solution in alkali reduces ammoniacal silver solution instantly in the cold. It does not give Liebermann's nitroso-reaction, but gives an intense red coloration with concentrated sulphuric acid and phenol or concentrated hydrochloric acid and β-naphthol.

It dissolves in cold concentrated hydrochloric acid to a yellow solution; on allowing this solution to stand for three days and then diluting with water, a yellow precipitate separated, which was crystallised from alcohol:

0·3310 gave 0·7262 CO_2 and 0·2086 H_2O. C = 59·86; H = 7·00.
0·1540 „ 10·35 c.c. moist nitrogen at 15·5° and 762 mm. N = 10·15.
$C_{21}H_{29}O_6N_3$ requires C = 60·14; H = 6·92; N = 10·02 per cent.

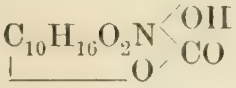
Hydroxylamine had therefore been eliminated in accordance with the equation:

$$C_{21}H_{32}O_7N_4 = C_{21}H_{29}O_6N_3 + NH_2{\cdot}OH.$$

An indication of the formation of hydroxylamine in this reaction
in the reduction of Fehling's solution by the filtrate.
issolves in hot alcohol to a pale yellow solution, but
in cold alcohol. Its solution in boiling benzene is
olves readily in glacial acetic acid to a yellow solu-
extent in boiling water, forming a deep yellow
wever, disappears on addition of a drop of

acid; with aqueous alkalis it forms deep yellow solutions, from which it separates on the addition of acids as a colourless precipitate.

The Lactonic Acid,



$$\begin{array}{l} C_{10}H_{16}O_2N\begin{array}{l}\diagup OH \\ \diagdown CO\end{array} \\ \lfloor\underline{\qquad\qquad\quad} O \diagup \end{array} .$$

When the base is heated with dilute acids it is slowly hydrolysed with formation of ammonia and a new nitrogenous acid. This acid is also formed when the lactam (L) or the amino-acid (A) is heated with dilute sulphuric acid, and on leaving the base (B) with a cold saturated hydrobromic acid. The hydrolysis of the base with hot dilute sulphuric acid was examined quantitatively. 1·12 Grams (1 mol.) of the base was heated on the water-bath with 20 c.c. of *N*-sulphuric acid (4 mols.) during one hour. On distilling with alkali, 0·88 mol. of ammonia was liberated.

For the preparation of the acid, a solution of the base (40 grams) in *N*-sulphuric acid (800 c.c.) was heated on the water-bath during two hours. On cooling, crystals separated, which were collected, washed with water, and dried by exposure to air. For analysis, the substance was crystallised from a mixture of chloroform and benzene and dried by exposure to air:

0·4708 gave 0·9382 CO_2 and 0·2984 H_2O. C = 54·35; H = 7·04.
0·3180 ,, 16·4 c.c. moist nitrogen at 16° and 750 mm. N = 5·93.
$C_{11}H_{17}O_5N$ requires C = 54·32; H = 7·00; N = 5·76 per cent.

0·7498 required 31·4 c.c. *N*/10 sodium hydroxide for neutralisation, whence the equivalent was 239; the number required for a monobasic acid, $C_{11}H_{17}O_5N$, is 243. It is readily soluble in hot water, alcohol, chloroform, acetic acid, ethyl acetate, or acetone, and sparingly so in cold water, carbon tetrachloride, benzene, or carbon disulphide. The acid when quite pure is colourless, but generally separates in the form of pale yellow crystals melting at 70—72°.

The crystals are thin, rectangular plates containing minute air bubbles, and having straight extinction in polarised light; occasionally, however, thick rhomboidal plates or rhombohedra are obtained, and in these the extinction directions approximately bisect the angles of the rhombs. Examined in convergent polarised light, some fragments show indistinctly one axis of a wide-angled interference figure. The double refraction is moderate, but its sign could not be determined.

0·6830 Gram dissolved and made up to 24·9 c.c. with absolute alcohol was examined in a 2-dcm. tube at 11°. The observed rotation was +2·06°, whence $[\alpha]_D$ +37·60°.

The acid is not altered by exposure to air, even during several months, but when placed in a vacuum desiccator over sulphuric acid it changes into a pasty mass. It reacts strongly acid to litmus and decomposes carbonates. On addition of ferric chloride to an aqueous solution of the acid, a dark blue colour is produced, which gradually disappears, a white, flocculent precipitate being formed. A neutral solution of the sodium salt gives with copper sulphate a deep yellowish-brown colour. It reduces ammoniacal silver nitrate, but does not affect Fehling's solution. A solution of the acid in acetic acid reacts instantly with bromine, even when excess of sodium acetate is present. An alkaline solution of the sodium salt is instantly oxidised by an ice-cold solution of potassium permanganate. On adding potassium permanganate to a solution of the acid in dilute sulphuric acid, a white, amorphous precipitate separates. Potassium dichromate and dilute sulphuric acid gives with an aqueous solution of the acid a pale yellow precipitate. This precipitate separates even from very dilute solutions of the acid. A similar precipitate is also formed when potassium ferricyanide is added to a solution of the acid in excess of sodium carbonate.

The acid dissolves readily in cold concentrated hydrochloric acid; on diluting the solution with water the unchanged acid was precipitated even after the liquid had been allowed to stand for four days.

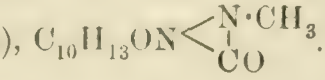
On boiling with concentrated hydrochloric acid it is decomposed with formation of ψ-cumenecarboxylic acid.

On boiling the acid with excess of sodium hydroxide and acidifying the cooled liquid, the unchanged acid separated, but on using a measured quantity of sodium hydroxide and estimating the excess of alkali it was found that a disodium salt had been formed.

1·215 after boiling with 25 c.c. *N*-sodium hydroxide required 15 c.c. *N*-sulphuric acid for neutralisation, whence the equivalent = 121·5; the number calculated for a dibasic acid, $C_{11}H_{17}O_5N$, is 121·5.

The acid is therefore an anhydro-derivative of a dibasic acid in which a carboxyl group is probably engaged in the formation of a lactone ring.

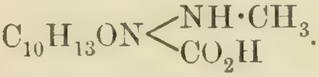
It reacts rapidly with sodium hydroxide and ferrous hydroxide, ammonia being evolved and ferric hydroxide produced.



The Methylated Lactam (LMe), $C_{10}H_{13}ON{<}\begin{matrix}N\cdot CH_3\\ |\\ CO\end{matrix}$.

A solution of equimolecular proportions of the lactam (L), methyl iodide, and sodium methoxide in absolute methyl alcohol was heated on the water-bath for three hours, after which water was added and the methyl alcohol expelled by a current of steam. The monomethyl derivative remained as a viscous, colourless oil which was insoluble in water, alkalis, or dilute mineral acids, and withstood all attempts to cause it to solidify. It was therefore not analysed, but converted directly into:

The Methylated Amino-acid (AMe),



$$C_{10}H_{13}ON<\substack{NH\cdot CH_3\\CO_2H}.$$

This was obtained by heating the preceding compound with eight times its weight of 10 per cent. sodium hydroxide on the water-bath for about two hours, when solution was complete. The liquid was then cooled and acidified, and the resulting crystalline powder recrystallised from dilute alcohol:

0·1241 gave 12·5 c.c. moist nitrogen at 16° and 767 mm. N = 11·9.
$C_{12}H_{18}O_3N_2$ requires N = 11·8 per cent.

0·807 required 33·7 c.c. of *N*/10 sodium hydroxide for neutralisation, whence the equivalent = 239, whilst a monobasic acid, $C_{12}H_{18}O_3N_2$, requires 238.

This compound is soluble in boiling water and separates almost entirely on cooling. It dissolves readily in alcohol, acetone, ethyl acetate, chloroform, or glacial acetic acid, sparingly in ether or benzene and is nearly insoluble in carbon disulphide or light petroleum. It melts at 155° and slowly decomposes at this temperature, evolving methylamine.

The crystals from dilute alcohol are transparent, truncated needles having straight extinction in polarised light, their direction of greatest elasticity and length being coincident. Crushed fragments examined in convergent polarised light show in some the acute bisectrix of an interference figure of moderate angle. The axial dispersion is moderately large, the angle for blue being greater than red light. The double refraction is strong and positive in sign.

This compound dissolves in cold dilute hydrochloric acid and the resulting solution does not give a precipitate on the addition of sodium nitrite, in which respect it differs from the non-methylated acid. It reduces warm ammoniacal silver solutions, and in faintly alkaline solution instantly discharges the colour of ice-cold potassium permanganate. It is apparently not changed when warmed with strong, aqueous sodium hydroxide on the water-bath, but if ferrous hydroxide is present a mixture of ammonia and methylamine is evolved, the iron compound being converted into ferric hydroxide; in a quantitative experiment which was not quite completed, one and one-third equivalents of base (ammonia and methylamine) were expelled; cyanide is not formed even in traces during this reaction. When the acid was treated with sodium hydroxide and ferrous hydroxide in the cold, ammonia with no trace of methylamine was evolved.

Action of Dimethyl sulphate and Alkali on the Amino-acid (A).

Both the original acid and its ester are further methylated when warmed with dimethyl sulphate and alkali in methyl-alcoholic solution, and prolonged heating causes the elimination of trimethylamine from the product. In an experiment where the mixture was heated for ten minutes only, the liquid was diluted, acidified, and mixed with a solution of iodine in potassium iodide, when an oily periodide was precipitated.

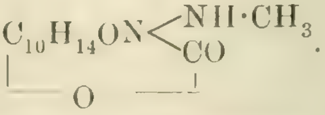
Some quantity of the periodide prepared in this way was decomposed by suspending it in water and passing sulphur dioxide into the warm liquid; the colour disappeared and a clear solution was obtained from which nothing could be isolated by extracting with any of the usual solvents. Finally, however, it was found that on adding concentrated aqueous potassium iodide and hydrochloric acid to the solution, an oily substance which slowly crystallised could be salted out, and this was collected and crystallised from chloroform:

0·4710 dissolved in water required 12·00 c.c. $AgNO_3$. I = 32·4.
0·2995 gave 0·3354 CO_2 and 0·1155 H_2O. C = 39·8; H = 5·6.
0·2100 ,, 12·2 c.c. moist nitrogen at 15° and 753 mm. N = 6·8.
$C_{13}H_{21}O_3N_2I,H_2O$ requires I = 32·7; C = 39·4; H = 5·3; N = 7·1 per cent.

The substance was boiled for some time with strong potassium hydroxide and the distillate collected in dilute hydrochloric acid; the contained base was proved, by analysis of its platinichloride (Pt = 39·4, $C_4H_{16}N_2Cl_6Pt$ requires Pt = 39·2 per cent.), to be dimethylamine, and the iodide from which it was obtained must therefore have been derived from a dimethylated acid. The product in the residual alkaline solution could not be obtained in a pure form.

These results indicate that the compound here dealt with was the hydriodide, $C_{10}H_{13}ON<\begin{smallmatrix}N(CH_3)_2\cdot HI\\CO_2H\end{smallmatrix}$, of the dimethylated acid.

The Methylated Lactonic Base (BMe),



$$C_{10}H_{14}ON<\begin{smallmatrix}NH\cdot CH_3\\CO\end{smallmatrix}.$$

The methylated amino-acid (AMe) (30 grams) was dissolved in cold concentrated hydrochloric acid (150 c.c.), a process which was accompanied by an appreciable rise in temperature. At the end of twenty-four hours the whole was exactly neutralised with sodium hydroxide. The oil which separated soon solidified to a crystalline mass, which was collected, washed, and crystallised from boiling water. The amount of base obtained was 28 grams:

0·1527 gave 15·5 c.c. moist nitrogen at 16° and 758 mm. N = 11·8.

$C_{12}H_{18}O_3N_2$ requires N = 11·8 per cent.

The compound resembles the non-methylated base (A) in solubility in various media and separates from boiling water in long crystals which melt at 129—130°.

The crystals are well formed, elongated, transparent plates through the larger faces of which the bisectrix of an interference figure of moderate axial angle passes perpendicularly. The double refraction is moderate and negative in sign.

For the determination of its optical activity, 0·6505 gram was dissolved and made up to 25·1 c.c. with absolute alcohol at 11° and the rotation examined in a 2-dcm. tube. The rotation observed was +0·37°, whence $[\alpha]_D$ +7·1°.

When a strong solution of the methylated base in hydrochloric acid is treated with sodium nitrite, a nearly colourless oil is precipitated, and no yellow precipitate is formed as is the case with the non-methylated base.

Action of Warm Dilute Acids on the Methylated Lactonic Base (BMe).

This base is not decomposed by 10 per cent. aqueous sodium hydroxide, but on warming with dilute acid for some time and subsequently with alkali, methylamine is liberated.

1·190 grams (1 mol.) of the methylated base were heated on the water-bath with 20 c.c. of *N*/2 sulphuric acid (2 mols.) during one and a half hours. On rendering the solution alkaline and distilling, methylamine (0·74 mol.) was liberated as determined by titration with *N*/5 hydrochloric acid. In a second experiment in which the heating lasted three hours, a larger amount of methylamine (0·95 mol.) was obtained. That methylamine and no ammonia was formed was proved by evaporating the neutralised distillate to dryness, when a crystalline, hygroscopic mass was obtained. This, under the polarising microscope, was found to be entirely composed of doubly refracting crystals; it was entirely soluble in absolute alcohol and after conversion into platinichloride gave the following analytical result:

0·3920 gave 0·0775 CO_2 and 0·0925 H_2O. C = 5·4; H = 2·6.

$C_2H_{12}N_2Cl_6Pt$ requires C = 5·1. H = 2·6 per cent.

The liquid from which the methylamine had been removed by distillation was acidified with sulphuric acid, and after remaining for twenty-four hours it deposited crystals which were collected and recrystallised from hot water. The substance obtained melted at 66—67°, and reacted with ferric chloride, copper sulphate, and potassium dichromate in exactly the same way as did the lactonic acid prepared from the unmethylated base (B). When mixed with the latter compound the melting point was 67—68°, so that the identity of the two compounds is beyond question.

Methylation of the Lactonic Base (B).

Dimethyl sulphate acts rapidly on this base at the ordinary temperature, heat being generated and an oily salt being produced. This is very readily soluble in water, but on treatment with alkali yields only an oily base which is apparently not identical with the methylated base (BMe). Solutions of the salt, even when highly dilute, yield a liquid periodide. Methyl iodide slowly forms a crystalline methiodide when heated with the base in a closed tube at 100°. This substance rapidly dissolves in water and the product appears to correspond with the methylated compound just described. Both substances, when heated with acids, furnish methylamine in considerable quantity.

Attempts were made to methylate the original base exhaustively by heating it with excess of dimethyl sulphate and alkali. Whilst considerable quantities of trimethylamine were formed, the other products were extremely soluble in water and were impossible to purify. They yielded ammonia when warmed with ferrous hydroxide and alkali.

Formation of 2:3:6-*Trimethylbenzoic Acid.*

The lactam (L) was heated during two days with four times its weight of concentrated hydrochloric acid on the water-bath; the originally colourless liquid gradually darkened and deposited a small quantity of a black oil, carbon dioxide being very slowly evolved. On cooling, the whole set to a mass of crystals consisting of ammonium chloride mixed with fine needles. This was collected, washed with water to remove inorganic matter, and finally extracted with dilute sodium carbonate solution. The filtered extract was acidified and the solid acid collected, washed, dried, and crystallised from petroleum; it contained no nitrogen:

0·2535 gave 0·6794 CO_2 and 0·1632 HO_2. C = 73·1; H = 7·2

$C_{10}H_{12}O_2$ requires C = 73·2; H = 7·3 per cent.

0·2079 required 12·1 c.c. $N/10$ NaOH for neutralisation, whence the equivalent = 166; the number calculated for a monobasic acid, $C_{10}H_{12}O_2$, being 164.

The acid, which can be obtained by similar treatment of any of the compounds convertible by acids into the lactonic acid (p. 989), dissolves freely in all the usual media with the exception of light petroleum and water, which dissolve it only when hot. It separates from hot light petroleum in small needles, and from hot water in long, silky, glistening needles. It is dimorphous, and when heated in a melting point tube fuses at 84° unless the temperature is raised too slowly, setting, almost at once, to a solid mass which melts at 105—106°.

The compound was found to be optically inactive in alcohol or ethyl acetate, and as it behaved as a saturated compound was evidently a benzene derivative.

Some quantity of the acid was therefore converted into its calcium salt and distilled with soda-lime under reduced pressure. An excellent yield of an hydrocarbon was obtained which was collected, dried over sodium, and distilled. The whole passed over between 166—168°, and on analysis:

0·1823 gave 0·6006 CO_2 and 0·1991 H_2O. C = 89·8; H = 12·1.

C_9H_{12} requires C = 90·0; H = 12·0 per cent.

The hydrocarbon agreed closely in properties with ψ-cumene, and in order fully to identify it the bromo- and nitro-derivative were prepared.

On analysis of the bromo-derivative:

0·1436 gave 0·2286 AgBr. Br = 66·5.

$C_9H_9Br_3$ requires Br = 66·9 per cent.

The substance crystallised in slender, white needles melting at 224—226° and agreed in all particulars with the tribromo-ψ-cumene obtained by Fittig and Laubinger (*Annalen*, 1869, **151**, 264).

Portions of the hydrocarbon were also nitrated and two nitro-derivatives obtained. One of these formed transparent, yellow needles melting at 70—71°, the other having a more slender habit and melting at 183—184°. These were evidently identical with the mono- and tri-nitro-ψ-cumenes obtained by Schäfer (*Zeitsch. für Chem.*, 1867, 12) and by Fittig and Laubinger respectively (*Annalen*, 1869, **151**, 261). There is thus no doubt that the hydrocarbon was ψ-cumene, and the acid from which it was prepared was therefore a nucleal ψ cumenecarboxylic acid. Two of the three possible acids of this type are known, namely, those with the structures $Me_3{:}CO_2H$ = 3 : 4 : 6 : 1 and 2 : 3 : 5 : 1. These melt at 149—150° and 127° respectively, so that the acid dealt with in the present instance is probably the hitherto unknown 2 : 3 : 6-trimethylbenzoic acid.

Much of the expense of this investigation was defrayed by a grant awarded by the Research Fund Committee of the Chemical Society for which the authors desire to express their indebtedness.

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XCIV.—*Studies of the Perhalogen Salts. Part I.*

By CHARLES KENNETH TINKLER, B.Sc.

IT has long been known that when iodine is dissolved in hydriodic acid or a solution of a metallic iodide, combination takes place between the iodine and iodide with the formation of a certain amount of periodide.

In 1877, a substance having the empirical formula KI_3 was isolated by Johnson (Trans., 1877, **31**, 249) from an aqueous-alcoholic solution of iodine and potassium iodide, whilst other metallic periodides have since been prepared. In addition a large number of periodides of organic bases have been described by Pelletier (*Annalen*, 1837, **22**, 113), Herepath (Trans., 1853, **5**, 177 and 1859, **11**, 130), Tilden (Trans., 1865, **18**, 99 and 1866, **19**, 145), Jörgensen (*Ber*., 1869, **2**, 460), and others.

Evidence of the formation of metallic periodides in nitrobenzene solution was obtained by Dawson (Trans., 1902, **81**, 524 and 1904, **85**, 796), who found that by shaking a mixture of iodine and metallic iodide with nitrobenzene, the iodine and iodide were dissolved in proportions which showed that substances of the type KI_3,BaI_6, &c., were produced when the iodide was in excess, and substances of the type KI_9,BaI_{18} when iodine was in excess. By substituting bromides and chlorides for iodides he obtained evidence of the formation of additive compounds of the halogen salt with iodine.

In connexion with an investigation on the state of iodine in various solvents, by an examination of the ultraviolet absorption spectra of its solutions, it was found that, whilst a $N/1000$ solution of iodine in water, chloroform, or alcohol shows no absorption band and very little general absorption in the ultraviolet when the thickness of layer photographed does not exceed 25 mm., on the addition of potassium iodide to $N/1000$ aqueous iodine the absorption spectra of the solution show very great general absorption and two absorption bands. Since potassium iodide itself in dilute solution has no characteristic absorption, the spectra of the solution of iodine in potassium iodide appear to be due to the presence of periodide. It thus appeared probable that the formation of these perhalogen salts in solution might be investigated by means of their ultraviolet absorption spectra.

(An account of the spectra of various iodine solutions is to be found in Kayser's *Handbuch der Spectroscopie*, **3**, 152 and 324.)

The spectra of $N/1000$ solutions of iodine in water containing excess of various iodides were photographed and were found in every case to be identical. In this connexion the iodides of sodium, potassium, barium, magnesium, cadmium, and aluminium were employed. Exactly similar spectra were also obtained on the addition of hydriodic acid, ammonium and tetramethylammonium iodides to the aqueous solution of iodine. In all cases the addition of the iodide produces a change in the visible colour of the solution from reddish-brown to yellow.

Since on the addition of all the iodides mentioned above exactly the same spectra were obtained, it seems probable that all these solutions of iodine contain the same ion, probably (I_3), as it has been shown by Janowkin (*Zeitsch. physikal. Chem.*, 1896, **20**, 19) and Dawson (Trans., 1901, **79**, 238) that a solution of iodine in potassium iodide contains the tri-iodide KI_3.

It was found by Dawson (Trans., 1904, **85**, 805) that cadmium iodide did not dissolve with iodine when the two substances were shaken with nitrobenzene, so that cadmium periodide was probably not produced under these conditions. The addition, however, of cadmium iodide to the aqueous solution of iodine gives a solution, the spectra of which are identical with those of solutions to which any of the above-mentioned iodides is added. Cadmium tri-iodide thus appears to exist in aqueous solution.

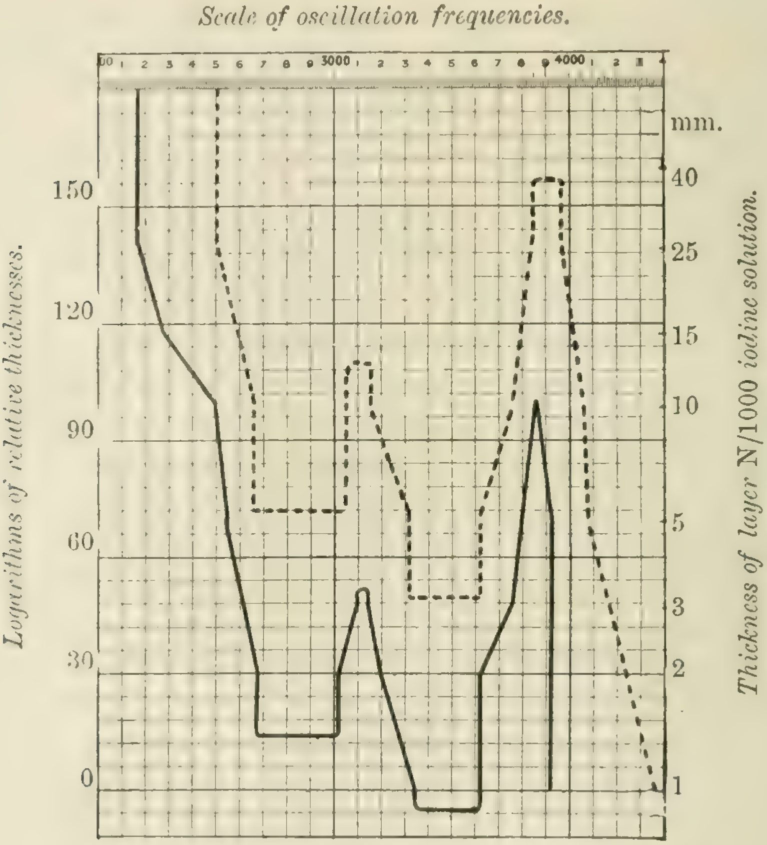
By means of the formula given by Dawson (Trans., 1902, **81**, 1090) it may be calculated that the amount of uncombined iodine in a *N*/1000 solution of iodine, containing 0·5 per cent. of potassium iodide, amounts to only approximately 1/30th of the total amount of iodine present. The absorption curve of such a solution is shown in Fig. 1. By increasing the amount of potassium iodide above 0·5 per cent., only a slight change is observed in the character of the spectra, apart from the absorption due to the iodide itself, although with increasing quantities of the iodide more periodide is produced. It appears to be easier to trace a slight increase in the amount of periodide by means of the spectra of the solution when the total amount of periodide is small than when it is great, as in the case of a solution containing 0·5 per cent. of potassium iodide. A somewhat similar result was observed in the case of the estimation of the relative amounts of the two forms of cotarnine in a solution of the substance in alkalis (Dobbie, Lauder, and Tinkler, Trans., 1904, **85**, 127 and Plate III, Trans., 1903, **83**, 605).

Fig. 1 shows the absorption curves of *N*/1000 solutions of iodine containing (i) 0·066 per cent. of potassium iodide and (ii) 0·5 per cent. of potassium iodide. By comparing the spectra of a solution of iodine containing a small quantity of an iodide with those of a solution containing an excess of the iodide, it is possible to estimate, although roughly, the amount of iodine in combination with the iodide. Thus, if the spectrum of a layer of a particular thickness of a solution of iodide containing a small quantity of an iodide is the same as a layer of, say, 1/5th the thickness of a solution containing excess of the iodide, it is probable that in the first solution approximately 1/5th of the iodine is in combination with the iodide.

The examination of the spectra of a solution of iodine in water to which a soluble bromide is added affords evidence of the formation of compounds of iodine and the bromide.

By again employing *N*/1000 aqueous iodine, a layer 25 mm. of which shows no absorption in the ultraviolet, on the addition of potassium bromide, spectra are obtained, which show one well marked absorption band and less general absorption than the spectra of iodine in a solution of an iodide. The same spectra were obtained by employing potassium bromide, magnesium bromide, cadmium bromide, hydrobromic acid, ammonium and tetramethylammonium bromides. The spectra are thus evidently characteristic of the same ion, which, owing to the large excess of bromide added and from analogy with the iodine additive compounds of iodides, is probably (BrI_2).

FIG. 1.

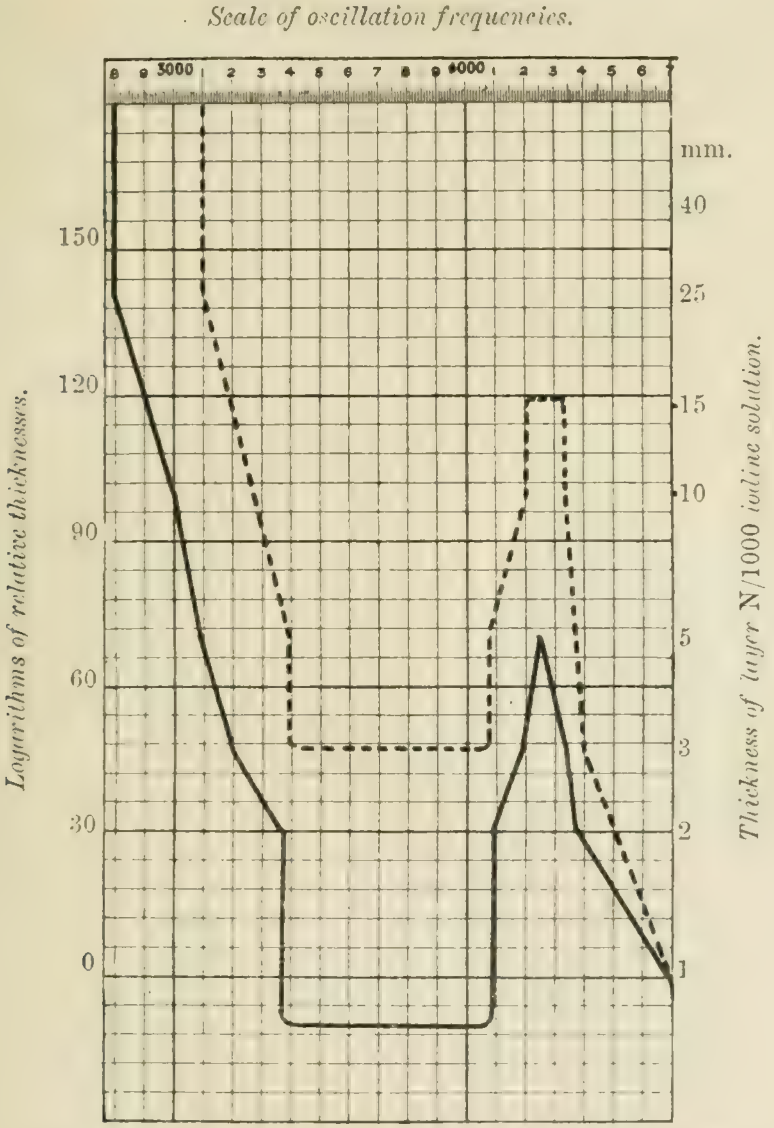


Dotted curve—N/1000-*Iodine in water* + 0·0066 *per cent.* KI.
Full ,, ,, ,, + 0·5 ,, KI.

Fig. 2 represents the absorption curves of *N*/1000 solutions of iodine containing 0·24 per cent. of potassium bromide and excess of the salt respectively.

As in the case of the iodides, it is possible to estimate the amount of iodine in combination with the bromide, assuming that with excess of bromide the whole of the iodine is in combination, which is extremely probable from the fact that when the solution contains a certain amount of bromide the addition of a further quantity causes no change in the absorption spectra. Thus, it will be seen from the curves, Fig. 2, a *N*/1000 solution of iodine containing 0·24 per cent. of potassium bromide gives spectra which are practically the same as those given by layers 2/5th the thickness when the solution contains

Fig. 2.



Dotted curve—N/1000-*Iodine in water* + 0·24 *per cent.* KBr.
Full ,, ,, ,, + *excess* KBr

excess of the salt. It appears therefore that in the first case approximately 2/5th of the iodine is in combination with the bromide.

The addition of a soluble chloride to the aqueous solution of iodine also causes a complete change in the character of the absorption; the spectra showing a well-defined absorption band and less general absorption than those of a solution of iodine containing a bromide. Exactly the same spectra were obtained by employing an excess of the chlorides of lithium, sodium, potassium, calcium, strontium, barium, magnesium, and aluminium, and also by hydrochloric acid, ammonium and tetramethylammonium chlorides. It appears therefore that in all these cases the same ion is produced, which from analogy with the iodide compounds is probably (ClI_2).

The absorption curve of these chloroperiodides is shown in Fig. 3.

The amount of iodine in combination with a given quantity of chloride can be estimated as in the two previous cases.

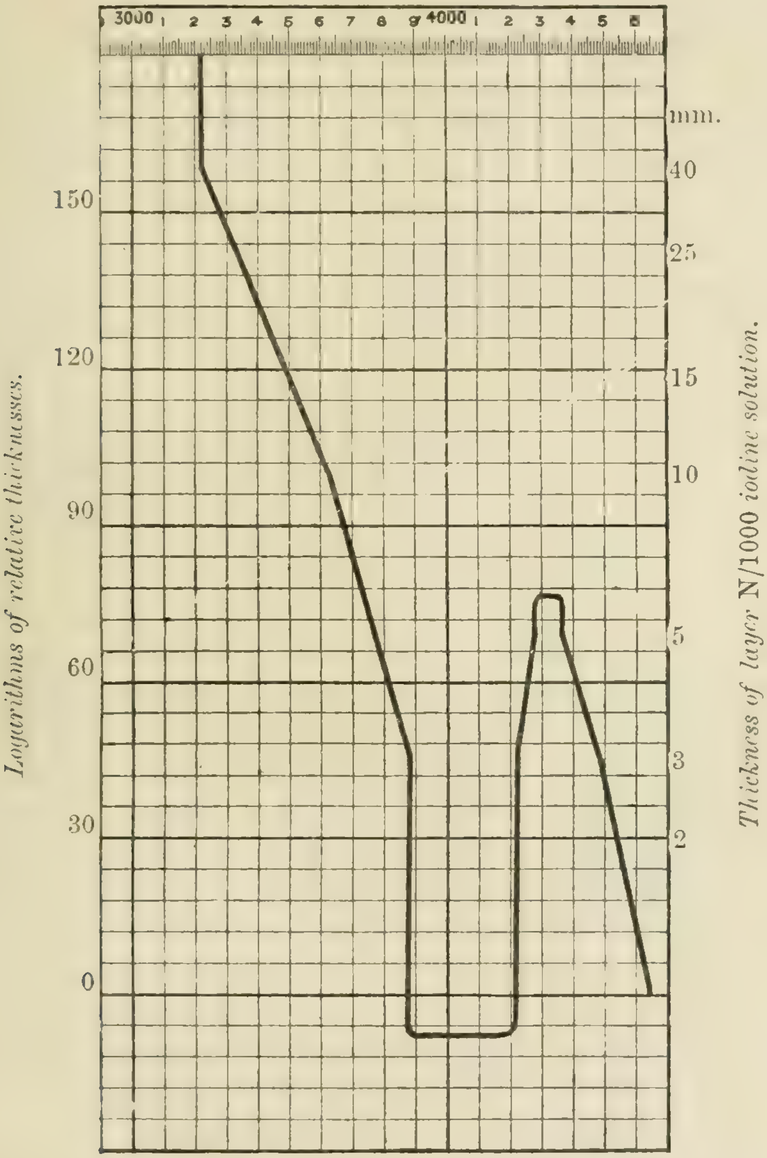
The addition of either a bromide or chloride to the aqueous solution of iodine also produces a slight change in the visible colour of the iodine solutions. By estimating the amount of combined iodine, from the spectra of a solution containing a haloid salt, it was found that the addition of a small quantity of potassium iodide effected combination of a much larger proportion of the iodine than is brought about by an equivalent quantity of potassium bromide or chloride. Thus, whilst in *N*/1000 solution of iodine containing 0·03 per cent. of potassium iodide, approximately one-half of the iodine appears to be in combination with the potassium iodide, a solution containing an amount of potassium bromide or potassium chloride equivalent to this amount of potassium iodide shows that only a very small quantity of the iodine has combined with the bromide, and practically no combination had taken place in the solution containing the chloride. It appeared therefore of interest to determine in what way the iodine would be distributed by employing a mixture of the halogen salts.

By the addition of mixtures containing equimolecular quantities of potassium iodide and bromide, iodide and chloride, and bromide and chloride to solutions of iodine it appeared from the spectra that almost the whole of the iodine combined with the salt of higher molecular weight. From these experiments and from the results obtained in estimating the amount of iodine which combines with equivalent quantities of potassium iodide, bromide and chloride added to separate solutions of iodine, it appears that the compound KI_3 is more stable in aqueous solution than $KBrI_2$ and $KClI_2$, and $KBrI_2$ more stable than $KClI_2$. It was also found by Dawson (*loc. cit.*) that in nitrobenzene solution combination of iodine and an iodide took place more readily than combination of iodine and a bromide or chloride.

Since the stability of the periodides seems to increase with the increase in molecular weight of the halogen salt in combination with the iodine, it might be expected that iodine would be more soluble in a solution of an iodide than in a solution of the corresponding bromide or chloride and more soluble in a solution of the bromide than in a solution of the chloride. The results of some preliminary experiments in this connexion appear to confirm this view. When equal volumes of equimolecular solutions of potassium iodide, bromide, and chloride are shaken with equal weights of iodine, under the same conditions,

FIG. 3.

Scale of oscillation frequencies.



N/1000-*Iodine in water + excess of* KCl.

the amounts of iodine dissolved by the respective solvents are greatest for the solutions of the iodide and least for the solutions of the chloride.

The same order of solubility was observed in the case of solutions of the corresponding ammonium salts, the solubility increasing with the stability of the perhaloid salt produced.

Since it was found that iodine combines more readily with an iodide than with either a bromide or chloride and with a bromide more readily than with a chloride, it might be expected that combination with a fluoride would take place less readily than with a chloride. By the addition of sodium, potassium, or ammonium fluorides no change is observed in the spectra, and it is probable that combination does not take place at all under the conditions of the experiment.

It is hoped to determine the relative stability of the iodine additive compounds of the various iodides in aqueous solution by the method previously described, and to apply the same method for determining the relative stability of the various bromoperiodides and of the chloroperiodides.

As already mentioned, it was found that by the addition of hydriodic, hydrobromic, or hydrochloric acids to the aqueous solution of iodine, the substances HI_3, $HBrI_2$, $HClI_2$ were probably produced; an investigation of the action of the corresponding gases on a chloroform solution of iodine was therefore undertaken in order to ascertain if such substances were formed in a non-ionising solvent. By passing dry hydrogen iodide into a *N*/1000 solution of iodine in chloroform, the colour of the solution changes from violet to yellow, and the ultraviolet absorption spectra of the solution obtained in this way are identical with those of a solution of iodine in water to which hydriodic acid or a soluble iodide has been added. It thus appears that the substance HI_3 is produced also in chloroform solution. A similar result was obtained by employing an alcoholic solution of iodine.

By passing a large excess of hydrogen iodide into the chloroform or alcoholic solution, the colour entirely disappears and the ultraviolet absorption spectra are again completely changed, spectra being obtained which show only slight general absorption. It is possible that under the influence of a large excess of hydrogen iodide the periodide reacts in some way with the solvent.

The spectra of a solution of iodine in chloroform through which hydrogen bromide or chloride has been passed do not show the pressure of the corresponding iodine additive compounds. The compounds of these acids are evidently less stable than the substance HI_3, as is the case of the additive compounds of the metallic salts in aqueous solution.

It was pointed out by Mylius (*Ber.*, 1887, 20, 688) that for the production of the blue colour of starch iodide in the well known test for iodine, it is necessary that hydriodic acid or a soluble iodide should be present with the reacting substances. He supposed that sufficient hydriodic acid is present in an aqueous solution of iodine for the production of a small quantity of starch iodide.

Meineke (*Chem. Zeit.*, 1894, **18**, 157) found that the formation of the blue starch iodide was also facilitated by the presence of a large quantity of other salts, such as sodium or potassium sulphates, the chlorides of various metals, &c., whereas the addition of a minute quantity of potassium iodide caused a great increase in the intensity of the blue colour when starch and an aqueous solution of iodine are mixed together.

Lonnes (*Zeitsch. anal. Chem.*, 1894, **32**, 33) suggested in explanation of the formation of starch iodide in the presence of a chloride, that a chloroiodide is produced, which is then transformed by the starch into an iodide, and this in turn facilitates the production of the starch iodide.

The absorption spectra of solutions of iodine to which a large amount of sodium sulphate or potassium sulphate have been added, show the presence of a very small quantity of a periodide, such as is obtained by the addition of a minute quantity of potassium iodide to the iodine solution. It has been shown by the ultraviolet absorption spectra of a solution of iodine containing a chloride that the chloride and iodine are in combination; it seems possible, therefore, from these preliminary experiments, that the production of the blue starch iodide is dependent on the presence of a periodide, the formation of which, however, in the case of salts such as sodium or potassium sulphate it is difficult to account for. It is possible that sufficient iodide is present as impurity in the added salt to give the reaction, since it can be shown that the addition of one-millionth of a gram of potassium iodide causes a visible increase in the intensity of the blue colour of an aqueous solution of iodine containing starch. The absorption spectra of solutions of iodine containing an iodide are completely changed on the addition of starch solution, the two absorption bands characteristic of the periodide no longer being observed.

Some preliminary experiments on the combination of bromine with bromides and with chlorides in aqueous solution have given results similar to those obtained in the case of iodine.

It is hoped to examine more fully, by this method, the formation of perhalogen salts and to investigate the effect of temperature on the stability of the compounds; all the experiments mentioned in this paper were carried out under the ordinary conditions, no special precautions being taken to ensure that the temperature of the various solutions was the same.

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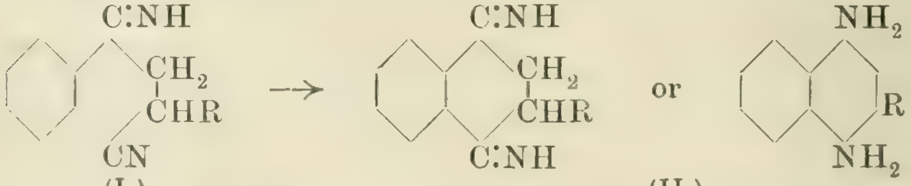
XCV.—*The Formation and Reactions of Imino-compounds. Part IV. The Formation of 1 : 4-Naphthylenediamine from Ethyl-γ-imino-α-cyano-γ-phenylbutyrate.*

By JOCELYN FIELD THORPE.

THE formation of derivatives of 1 : 3-naphthylenediamine by the action of cold concentrated sulphuric acid on imino-nitriles having the imino-group in the β-position and the cyano-group in the α-position in respect to a phenyl group has been established in Part II of this series (Trans., 1906, 89, 1906), whereas in Part III (Trans., 1907, 91, 578) the formation of similar derivatives from compounds containing a methyl group in the ortho-position in a benzene ring to a side-chain of two carbon atoms having an imino-group attached to the β-carbon atom and a cyano-group to the α-carbon atom was also proved.

In the present paper it is shown that derivatives of benzene having a side-chain of three carbon atoms substituted at the α-carbon atom by a nitrile group and at the γ-carbon atom by the imino-group (I) pass on treatment with strong sulphuric acid into derivatives of 1 : 4-naphthylenediamine (II); ring formation taking place between the ortho-hydrogen atom of the benzene ring in respect to the side-chain and the carbon atom of the nitrile group. The general formula for this third reaction can therefore be represented as follows:

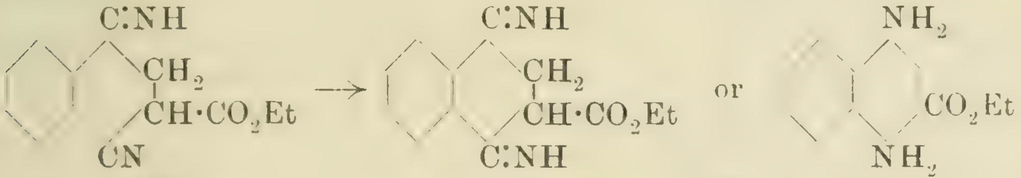


(I.) (II.)

Unfortunately the methods described in the previous communications for the formation of imino-compounds could not be applied for the preparation of a compound of type (I), since the imino-group in this case is attached to the γ-carbon atom and not to the β-carbon atom of the side-chain.

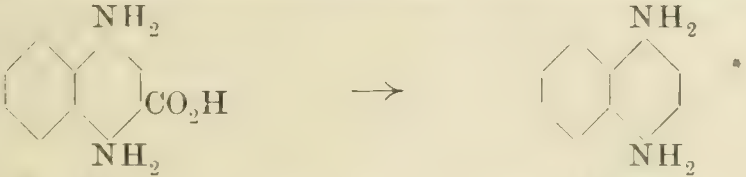
This difficulty will be realised when it is mentioned that in spite of many attempts it has not been found possible to prepare, by direct condensation, imino-nitriles containing the imino-group in a position other than that which is the β-position in respect to the nitrile group. Recourse was therefore had to the method of preparing the imino-compound from the corresponding ketone by the aid of ammonium acetate, a process which was adopted with partial success in Part III of this series for the preparation of ethyl β-imino-α-cyano-β-*o*-tolylpropionate.

Ethyl α-cyano-γ-keto-γ-phenylbutyrate, $COPh{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$, has been prepared by Klobb (*Ann. Chim. Phys.*, 1897, [vii], 10, 179) by the action of ω-bromoacetophenone on the sodium compound of ethyl cyanoacetate. This ethyl salt when treated with ammonium acetate is converted to the extent of about 50 per cent. into ethyl γ-imino-α-cyano-γ-phenylbutyrate (III), which, on treatment with cold concentrated sulphuric acid, is quantitatively converted into ethyl 1 : 4-naphthylenediamine-3-carboxylate (IV) in accordance with the scheme:



(III.) (IV.)

This ethyl salt, which is a pale yellow, crystalline compound, is transformed on alkaline hydrolysis into 1 : 4-naphthylenediamine-3-carboxylic acid (V), which in its turn is converted into 1 : 4-naphthylenediamine (VI) on heating at 200° in an atmosphere of hydrogen.



(V.) (VI.)

The base prepared in this way possessed all the properties of 1 : 4-naphthylenediamine and was further identified by its conversion into α-naphthaquinone on treatment with nitrous acid.

Preparation of Ethyl α-cyano-γ-keto-γ-phenylbutyrate (Ethyl Phenacylcyanoacetate), $COPh{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$.

The main difficulty experienced in preparing this substance in any quantity from ω-bromoacetophenone and the sodium derivative of ethyl cyanoacetate was due to the fact noticed by Klobb (*loc. cit.*) that when the condensation is carried out in the ordinary way a considerable proportion of the product consists of ethyl diphenacylcyanoacetate, which has been formed by the interaction of two molecular proportions of ω-bromoacetophenone and one molecular proportion of ethyl sodiocyanoacetate.

The formation of this compound is evidently due to the interaction of the initial condensation product (ethyl phenylcyanoacetate) and the sodium compound of ethyl cyanoacetate causing the regeneration of ethyl cyanoacetate, the sodium derivative then reacting with ω-bromoacetophenone to form ethyl diphenacylcyanoacetate.

The formation of the diphenacyl derivative can be, however, almost entirely prevented if the method is adopted of using two molecular proportions of the sodium derivative to one of the bromo-compound. The reaction then proceeds directly in accordance with the equation:

$$2CHNa(CN){\cdot}CO_2Et + COPh{\cdot}CH_2Br = COPh{\cdot}CH_2{\cdot}CNa(CN){\cdot}CO_2Et + CN{\cdot}CH_2{\cdot}CO_2Et.$$

Twenty-three grams of sodium were dissolved in 270 grams of absolute alcohol and the solution mixed with 113 grams of ethyl cyanoacetate. One hundred grams of ω-bromoacetophenone dissolved in the least quantity of alcohol were then added gradually to the well-cooled sodium derivative, the vigorous reaction being checked by cooling under running water. When all the bromo-compound had been added, the mixture was allowed to stand at the ordinary temperature for half an hour, when it was heated on the water-bath for two hours in order to complete the reaction. Dilute hydrochloric acid was then added and the oil which separated extracted by means of ether. The ethereal layer when separated from the aqueous solution contained some insoluble substance in suspension. This was collected and crystallised from alcohol, yielding colourless prisms melting at 173°, evidently therefore consisting of ethyl diphenacylcyanoacetate originally prepared by Klobb (*loc. cit.*). The quantity of this compound was, however, very small and the weight of the crude product scarcely exceeded 5 grams. The filtered ethereal solution was dried and evaporated free from ether, leaving a dark coloured oil which consisted of ethyl phenacylcyanoacetate and ethyl cyanoacetate, formed in accordance with the equation previously given. The presence of ethyl cyanoacetate prevented the condensation product from crystallising, and, since a separation could not be effected by distillation owing to the fact that ethyl phenacylcyanoacetate cannot be distilled without undergoing decomposition, recourse was had to the following method of separation which depended on the property possessed by ethyl cyanoacetate of forming a sodium compound which does not regenerate the ethyl salt on treatment with water or dilute acids (compare Thorpe, Trans., 1900, 77, 925).

The condensation product containing ethyl cyanoacetate was added to excess of sodium ethoxide dissolved in alcohol and the mixture treated with a large quantity of dilute hydrochloric acid; the oil which then separated completely solidified on standing and was isolated by filtration. It was purified by crystallisation from ether and obtained in colourless, lustrous plates melting at 54°:

0·2019 gave 0·4982 CO_2 and 0·1048 H_2O. C = 67·29 ; H = 5·76.

$C_{13}H_{13}O_3N$ requires C = 67·5 ; H = 5·6 per cent.

Formation of Ethyl γ-Imino-α-cyano-γ-phenylbutyrate $NH{:}CPh{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$.

Some little difficulty was experienced in discovering the most favourable conditions for the formation of this imino-compound from the ketone by fusion with ammonium acetate. After numerous trials it was ultimately found that the success of the experiment depended on the absence of water from the ammonium acetate used and that the presence of even traces of moisture almost entirely prevented the formation of the ethyl imino-salt. Care was always taken therefore to fuse the ammonium acetate for some time previous to use.

Twenty grams of ethyl phenacylcyanoacetate were dissolved in 100 grams of melted ammonium acetate and the clear solution heated to boiling on the sand-bath for fifteen minutes. On pouring the fused mass into five times its volume of water a white precipitate separated, which considerably increased on standing. It was collected by the aid of the pump and crystallised from absolute alcohol, being obtained in long needles melting at 143° :

0·2121 gave 0·5281 CO_2 and 0·1199 H_2O. C = 67·90 ; H = 6·28.

0·2592 ,, 26·0 c.c. of nitrogen at 12° and 770 mm. N = 12·15.

$C_{13}H_{14}O_2N_2$ requires C = 67·8 ; H = 6·1 ; N = 12·2 per cent.

Ethyl γ-imino-α-cyano-γ-phenylbutyrate is practically insoluble in benzene or light petroleum and is sparingly soluble in cold alcohol or cold ether. Either of these last named solvents can be used for recrystallisation. The yield of the imino-compound obtained by this means is about 50 per cent. of the theoretical amount.

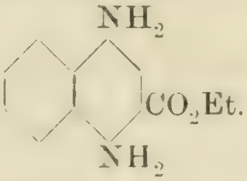
The ethyl salt is not acted on by strong aqueous alkalis or by dilute acids in the cold, but is slowly hydrolysed on boiling. In order to establish its constitution 5 grams were boiled in a Geissler flask with dilute hydrochloric acid until all had passed into solution. On cooling, a crystalline substance separated, which after being collected and recrystallised from water melted at 116° :

0·1999 gave 0·4935 CO_2 and 0·1036 H_2O. C = 67·33 ; H = 5·75.

$C_{10}H_{10}O_3$ requires C = 67·4 ; H = 5·6 per cent.

The properties of this compound are in complete accordance with those of β-benzoylpropionic acid, $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

Formation of Ethyl 1 : 4-*Naphthylenediamine-3-carboxylate*,



The transformation of ethyl γ-imino-α-cyano-γ-phenylbutyrate into the above naphthalene derivatives takes place with the same ease as that recorded in the case of the other condensations already investigated, the change being complete after the imino-compound has remained in contact with cold strong sulphuric acid for three minutes.

Ten grams of ethyl γ-imino-α-cyano-γ-phenylbutyrate were gradually added to 30 grams of well-cooled concentrated sulphuric acid. As the imino-compound passed into solution the strong acid became olive-green, and when all had dissolved and the solution had stood for three minutes it had become coloured deep malachite-green. The strong acid solution was then slowly poured into ten times its volume of well cooled absolute alcohol, when a white solid separated which was collected, washed with a little alcohol, and dried. An analysis proved this substance to be the *sulphate* of *ethyl* 1 : 4-*naphthylenediamine*-3-*carboxylate*, $C_{13}H_{14}O_2N_2,H_2SO_4$:

0·2318 gave 0·1640 $BaSO_4$. $S = 9·71$.

$C_{13}H_{14}O_2N_2,H_2SO_4$ requires $S = 9·8$ per cent.

The sulphate is readily soluble in cold water, but can be crystallised from its aqueous solution on concentration, when it separates in small, lustrous plates usually slightly coloured.

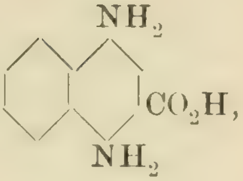
An aqueous solution of the sulphate gives a lemon-yellow precipitate of the *free base* on being rendered alkaline with ammonia. It was collected, dried, and crystallised from ether, from which solvent it separated in small, lemon-yellow needles melting at 119°:

0·1908 gave 0·4717 CO_2 and 0·1071 H_2O. $C = 67·42$; $H = 6·23$.

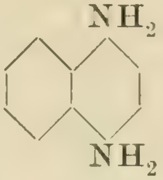
$C_{13}H_{14}O_2N_2$ requires $C = 67·8$; $H = 6·1$ per cent.

The *hydrochloride*, $C_{13}H_{14}O_2N_2,2HCl$, is obtained as a white, crystalline precipitate on adding concentrated hydrochloric acid to a solution of the base in absolute alcohol. It is readily soluble in water, but is practically insoluble in cold concentrated hydrochloric acid.

Formation of 1 : 4-*Naphthylenediamine-3-carboxylic Acid*,



and 1 : 4-*Naphthylenediamine*,



The hydrolysis of ethyl 1 : 4-naphthylenediamine-3-carboxylate was effected by warming five grams with a methyl-alcoholic solution of one and a half times the calculated quantity of potash, when, just as in the analogous case of the 1 : 3-derivative, the formation of an insoluble potassium salt rendered the isolation of the free acid in a pure condition an easy matter. As soon as the formation of the *potassium* salt appeared to be complete it was filtered by the aid of the pump, washed with a little methyl alcohol, and dried. It consisted of a pale yellow, crystalline substance readily soluble in water :

0·2101 gave 0·0758 K_2SO_4. K = 16·18.
$C_{11}H_9O_2N_2K$ requires K = 16·3 per cent.

An aqueous solution of the potassium salt gave a white precipitate on treatment with dilute hydrochloric acid, and this, on crystallisation from hot water, yielded the *free acid* in colourless plates, which decomposed, apparently without melting, at about 185° :

0·2214 gave 9·5268 CO_2 and 0·1043 H_2O. C = 64·89 ; H = 5·23.
$C_{11}H_{10}O_2N_2$ requires C = 65·3 ; H = 4·9 per cent.

The acid is practically insoluble in cold water.

The carboxylic acid was converted into 1 : 4-naphthylenediamine by heating it in a current of hydrogen to 200°.

The finely-powdered acid was placed in a wide-mouthed tube fitted with an arrangement by which the air could be completely replaced by dry hydrogen. The tube was heated in a bath of sulphuric acid at the required temperature until the evolution of gas had ceased ; dilute hydrochloric acid was then added and the solution filtered to remove any unchanged acid. The solution of the hydrochloride, which had a red colour, gave a precipitate of the free base on being made alkaline by means of ammonia. The base was then rapidly filtered and crystallised from hot water, being obtained in white needles melting at 120°. The compound rapidly oxidised on exposure to the air :

0·1784 gave 0·4973 CO_2 and 0·1002 H_2O. C = 76·02 ; H = 6·24.
$C_{10}H_{10}N_2$ requires C = 76·0 ; H = 6·3 per cent.

The base was in all respects identical with the well known 1 : 4-naphthylenediamine. It was further characterised by its conversion into its diacetyl derivative, which was found to melt at 304—305° (compare Kleemann, *Ber.*, 1886, **19**, 334; Bamberger and Schieffelin, *Ber.*, 1889, **22**, 1381).

The conversion of base into α-naphthaquinone was effected according to the method described by Grandmougin and Michel (*Ber.*, 1892, **25**, 977). One gram was dissolved in excess of dilute hydrochloric acid, and after the solution had been cooled to 5° it was mixed with excess of a solution of sodium nitrite. Gas was evolved and a yellow precipitate of the quinone separated. It was collected and crystallised from alcohol, yielding sulphur-yellow crystals melting at 125°.

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XCVI.—*Some Compounds of Guanidine with Sugars. Part I.*

By R. S. MORRELL and A. E. BELLARS.

THE action of ammonia on sugars has been investigated by Lobry de Bruyn in conjunction with van Leent and Alberda van Ekenstein (*Rec. trav. chim.*, 1893, **12**, 286; 1894, **13**, 218; 1895, **14**, 98 and 134). They showed that ammonia reacted slowly with sugars in methyl-alcoholic solution to give "osamines," for example, $C_6H_{13}O_5N$, or in the case of lactose a simple addition product of the carbohydrate with ammonia was formed.

Compounds of lime and lead monoxide with mono- and disaccharides are well-known substances.

Several years ago one of us in investigating the action of organic bases on glucosone tried the action of guanidine on it. On mixing alcoholic solutions of the two substances, a white, amorphous precipitate was obtained which seemed to contain two molecules of guanidine with one molecule of glucosone.

On addition of an alcoholic solution of guanidine, prepared from guanidine carbonate, to alcoholic solutions of dextrose, lævulose, or mannose, white, microcrystalline precipitates were obtained which were extremely hygroscopic. Alcoholic solutions of galactose, rhamnose, arabinose, or maltose gave with guanidine similar precipitates.

Dextrose guanidine had been obtained by Herzfeld (*Zeitsch. Ver. deut. Zuckerind.*, 1895, **45**, 853), but not in a pure state, and further investigation of these guanidine compounds seemed to be of interest.

The guanidine used in the preparation of guanidine sugar compounds was obtained from the carbonate by treatment with less than the calculated quantity of barium hydroxide; after filtration from barium carbonate, the aqueous solution of guanidine was concentrated under reduced pressure at 40° to a thick syrup; the syrup was dissolved in absolute alcohol, filtered from guanidine carbonate, and allowed to flow drop by drop into a solution of a sugar in 98 per cent. ethyl alcohol. In almost every case the guanidine compound separated as a white, minutely crystalline substance. After a few hours the precipitate was filtered off, washed with absolute alcohol, afterwards with dry ether, and dried in a vacuum over phosphoric oxide. The yield was generally excellent. In one experiment 18 grams of dextrose dissolved in 1500 c.c. of 98 per cent. alcohol gave nearly 22 grams of the compound, this being the calculated amount for dextrose guanidine of the formula $3C_6H_{12}O_6,2CH_5N_3$. From 18 grams of lævulose 13 grams of lævulose guanidine were obtained. A portion of the lævulose guanidine is generally precipitated immediately, and the remainder separates after several hours.

The compounds of guanidine with mannose, lævulose, and dextrose are very hygroscopic; they are insoluble in all solvents except methyl alcohol or water, but from these solvents it is impossible to obtain them in a crystalline form owing to secondary changes in the solutions, which will be referred to later. The substances were analysed as precipitated, constancy of composition on analysis of several samples prepared by using varying quantities of guanidine being the only possible guarantee of their purity.

Dextrose guanidine:

0·1948 gave 0·2613 CO_2 and 0·129 H_2O. C = 36·59; H = 7·35.

0·1748 ,, 19 c.c. moist nitrogen at 15° and 767 mm. N = 12·57.

0·8995, prepared by using a large excess of guanidine, required 24·7 c.c. *N*/10 HCl. CN_3H_5 = 17·97.

1·335 dissolved in 20 c.c. *N*-hydrochloric acid required 41 c.c. *N*/10 sodium hydroxide for neutralisation. CN_3H_5 = 18·0.

1·051 gave 0·8494 guanidine picrate. CN_3H_5 = 17·5.

$3C_6H_{12}O_6,2CH_5N_3$ requires C = 36·47; H = 6·99; N = 12·76; CH_5N_3 = 17·9 per cent.

Picric acid can be used to estimate the guanidine, if the correction for the solubility of guanidine picrate in water (Emich, *Monatsh.*, 1892, **12**, 24) is introduced.

Lævulose guanidine:

0·1757 gave 0·2378 CO_2 and 0·1173 H_2O. C = 36·9; H = 7·41.

0·1500 gave 16·6 c.c. moist nitrogen at 14° and 755 mm. N = 12·92.

0·7890 dissolved in 10 c.c. *N*-hydrochloric acid required 76·4 c.c. *N*/10 sodium hydroxide. $CH_5N_3 = 17·6$.

$3C_6H_{12}O_6,2CH_5N_3$ requires C = 36·47. H = 6·99 ; N = 12·76 ; $CH_5N_3 = 17·9$ per cent.

Mannose guanidine :

0·1725 gave 0·2300 CO_2 and 0·1117 H_2O. C = 36·36 ; H = 7·19.

0·1885 ,, 21·5 c.c. moist nitrogen at 17° and 756 mm. N = 13·16.

0·3516 required 10·6 c.c. *N*/10 hydrochloric acid. $CH_5N_3 = 17·78$.

$3C_6H_{12}O_6,2CH_5N_3$ requires C = 36·47. H = 6·99 ; N = 12·76 ; $CN_3H_5 = 17·9$ per cent.

These compounds on being heated for some time to about 50° in a vacuum over phosphoric oxide become yellow, but they can be dried at 40° without change in composition. They have no sharp melting points; below 100° they fuse with effervescence; dextrose guanidine at 94°, lævulose guanidine at 90°, mannose guanidine at 80°. When dextrose guanidine was heated to 100° for several hours, the alkaline reaction disappeared, and the substance no longer reduced Fehling's solution, but it gave phenylglucosazone when warmed with phenylhydrazine acetate. The residue on analysis contained C = 40·9 ; H = 6·5, and N = 14·7. $3C_6H_{12}O_6,2CH_5N_3 - 4H_2O$ requires C = 40·95 ; H = 6·48 ; N = 14·3 per cent. We have not investigated this substance further.

From the heat of neutralisation of guanidine by nitric acid (Matignon, *Ann. Chim. Phys.*, 1893, [vi], **28**, 88), namely, 14·12 C per gram-molecule, and the electrical conductivity as determined by Ostwald (*J. pr. Chem.*, 1886, [ii], **33**, 367), guanidine is a stronger base than tetramethylammonium hydroxide, and very nearly as strong as caustic soda and baryta. This conclusion we have confirmed by applying three other methods, (*a*) by observing the velocity of the fall in angle of a hyoscyamine solution in the presence of guanidine (Witt and Bredig, *Ber.*, 1888, **21**, 2777); (*b*) by measuring the velocity of saponification of ethyl acetate by the free base; (*c*) by measuring the depression of the freezing point of an aqueous solution of guanidine. In these experiments the influence of the guanidine was compared with that of sodium hydroxide or baryta of equivalent strength.

(*a*). Hyoscyamine + *N*-sodium hydroxide. $t = 20°$.

Mins.	$[\alpha]_D^{20°}$.	$K = 1/t \log \frac{[\alpha]_0^D - [\alpha]_\infty^D}{[\alpha]_t^D - [\alpha]_\infty^D}$.
0	−20·32°	—
5¼	17·94	0·0114
8½	17·14	0·0096
13¼	15·45	0·0103
21½	12·97	0·0102
28¾	11·19	0·0103
39¼	9·32	0·0100
50	7·64	0·0101
64	6·48	0·0098
∞	1·86	0·0103 mean

Hyoscyamine + *N*-guanidine solution. $t = 20°$.

Mins.	$[\alpha]_D^{20°}$.	$K = 1/t \log \frac{[\alpha]_0^D - [\alpha]_\infty^D}{[\alpha]_t^D - [\alpha]_\infty^D}$.
0	−20·32°	—
8	17·79	0·0080
9	17·28	0·0087
10	17·11	0·0083
16½	15·18	0·0086
27	13·34	0·0076
35	11·74	0·0078
45	10·06	0·0078
∞	1·86	0·0081 mean

Sodium hydroxide : guanidine = 1 : 0·78.

In two other experiments the $[\alpha]_D$ values for sodium hydroxide and guanidine with hyoscyamine were found to be practically the same, and the ratios were 1 : 0·72. Experiments using 2*N*-solutions of the bases gave the ratio 1 : 0·76.

(*b*) Velocity of saponification of ethyl acetate by sodium hydroxide, baryta, and guanidine.

a = c.c. of *N*/20-alkali originally present. x = c.c. of *N*/20-alkali disappeared.

N/20 Sodium hydroxide and *N*/20 ethyl acetate. $t = 20°$.

Mins.	$a - x$.	x.	ak.
0	25·0	0·0	—
3	18·3	6·7	0·121
6	15·0	10·0	0·111
9	12·0	13·0	0·120
12	10·7	14·3	0·111
15	9·5	15·5	0·109
18	8·55	16·45	0·107
21	7·65	17·35	0·108
24	6·9	18·1	0·109
		Mean	0·112

N/20 Guanidine and *N*/20 ethyl acetate. $t = 20°$.

Mins.	$a - x$.	x.	ak.
0	25·0	0·0	—
3	19·5	5·5	0·0940
6	15·65	9·35	0·0995
9	13·3	11·7	0·0985
12	11·65	13·35	0·0955
15	10·3	14·7	0·0951
18	9·3	15·7	0·0938
21	8·4	16·6	0·0941
24	7·9	17·1	0·0902
		Mean	0·0951

Several determinations of the velocity of saponification of ethyl acetate were made, and the ratios of strengths of sodium hydroxide or baryta and guanidine were: Sodium hydroxide : guanidine = 1 : 0·85; baryta : guanidine = 1 : 0·926.

(*c*) *Depression of the Freezing Point of an Aqueous Solution of Guanidine.*—The guanidine solution was prepared by the action of baryta water on an aqueous solution of purified guanidine sulphate of correctly equivalent strength. The caustic soda was the same as that used in the two previous methods.

The depression of the freezing point for a *N*/2 guanidine solution was found to be −1·67° (mean of four determinations, each with fresh samples of guanidine prepared from three different samples of guanidine sulphate).

The depression of the freezing point for a *N*/2 sodium hydroxide solution was − 1·838° (mean of several determinations of separate and new solutions of freshly prepared *N*/2 sodium hydroxide).

If the *N*/2 sodium hydroxide be considered as containing completely dissociated molecules, the strength of guanidine as a base compared with sodium hydroxide will be $\frac{1{\cdot}67 - 0{\cdot}919}{0{\cdot}919} = 0{\cdot}81$.

This agrees fairly well with the results obtained by the hyoscyamine and saponification methods.

The Properties of Aqueous Solutions of the Compounds of Guanidine with Sugars.

Since the compounds of guanidine with sugars are decomposed by water, it seemed of interest to investigate whether they were completely resolved into their components in aqueous solution or not. We have determined the freezing points for aqueous solutions of dextrose and guanidine mixed in the proportions of three to two, and the freezing points of similar solutions of fructose and guanidine.

The following table gives the results of a number of determinations:

Depression of Freezing Points.

N/2-Guanidine.	*N*/2-Caustic soda.	*N*/2-Dextrose.	*N*/2-Lævulose.	3 c.c. *N*/2-Dextrose, 2 c.c. *N*/2-guanidine.	3 c.c. *N*/2-Lævulose, 2 c.c. *N*/2-guanidine.	Calculated depression.
−1·67°	—	−1·01°	—	−0·93°	—	−1·274°
−1·67	—	—	−1·02°	—	−0·97°	−1·28
				3 c.c. *N*/2-Glucose, 2 c.c. *N*/2-Caustic soda.	3 c.c. *N*/2-Fructose, 2 c.c. *N*/2-Caustic soda.	
—	−1·838°	−1·01°	—	−0·89°	—	−1 341°
—	−1·838	—	−1·02°	—	−0·95°	−1·347

The calculated depression is obtained by taking the sum of $\frac{2}{5}$ × 1·67° + $\frac{3}{5}$ × 1·01° = 1·274° for dextrose guanidine, and similarly for the other compounds. From these data it is evident that guanidine forms a compound with dextrose or lævulose in aqueous solution.

H. Euler (*Ber.*, 1905, 38, 2551; 1906, 39, 350) came to similar conclusions as to the acidic nature of aldehydes from the study of the freezing points of normal and semi-normal solutions of sodium hydroxide, dextrose, formaldehyde, and acetaldehyde.

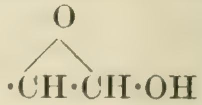
From the freezing points of aqueous solutions of guanidine dextrose and lævulose compounds, the molecular weights were found to be 122 and 118·6 respectively. The calculated molecular weight of the solid compound is 658. Complete dissociation in solution would furnish per molecule 7 parts, namely: 3 dextrose, 2 (CN_3H_5H), and 2 $(OH)'$, but guanidine is only dissociated to the extent of 80 per cent., therefore the calculated molecular weight of the compounds in solution will be $\frac{658 \times 100}{7 \times 80} = 117{\cdot}5$. The observed values agree exceedingly well with this number.

In aqueous solution the compounds show decided mutarotation to an equilibrium value. It was found that the initial specific rotation was dependent on the age of the specimen examined, although the composition remained unaltered. It is thought that the solid substance undergoes slow isomeric change on standing in a vacuum. In the case of dextrose guanidine a freshly prepared specimen has a specific rotation $[\alpha]_D$ $+31{\cdot}47°$, whilst older specimens have $[\alpha]_D$ $+29°$ and even $+22{\cdot}95°$. A freshly prepared mannose guanidine has $[\alpha]_D$ $+10{\cdot}03°$, the same specimen several days later $[\alpha]_D$ $+8{\cdot}81$. In the case of lævulose guanidine, the initial specific rotation varies between $[\alpha]_D$ $-62{\cdot}21°$, $[\alpha]_D$ $-53{\cdot}3°$, and $[\alpha]_D$ $-38{\cdot}84°$. The influence of concentration and temperature and the slow isomeric change which sets in when an aqueous solution is examined make an absolute uniformity of values impossible.

The gradual isomeric change of one sugar into another by the action of free alkali was first investigated by Lobry de Bruyn and Alberda van Ekenstein (*Rec. trav. chim.*, 1895, **14**, 18). They showed a partial reciprocal transformation of dextrose into lævulose and mannose in which lævulose was the intermediate substance in the change according to the scheme:

$$\text{dextrose} \longleftrightarrow \text{lævulose} \longleftrightarrow \text{mannose.}$$

Acids, probably saccharinic and other sugars, for example ψ-lævulose and glutose, were formed (*loc. cit.*, 1897, **16**, 262). By boiling a 20 per cent. aqueous solution of dextrose with $2\frac{1}{2}$ per cent. aqueous caustic potash for five minutes, the composition of the mixture of sugars was given as 49 per cent. dextrose, 5 per cent. mannose, and 28 per cent. lævulose. The percentage of lævulose was considered to be too high owing to the presence of isomeric ketoses. At the ordinary temperature an aqueous solution of 10 per cent. dextrose containing 2·8 per cent. aqueous caustic potash had its rotatory power changed in 117 hours from +42° to −3·5° with the disappearance of 60 per cent. of the alkali.

In the presence of lime the fall in the rotatory power at the ordinary temperature was more rapid and no mannose was formed. The mechanism of the change was explained by the combination of a molecule of water with the aldehydic or ketonic groups of the sugar and subsequent loss of water to form the group  $\cdot\overset{O}{\overbrace{CH\cdot CH}}\cdot OH$, which is probably capable of existing in two forms. This complex is converted by intramolecular transposition partly into lævulose

$$\cdot CO\cdot CH_2\cdot OH,$$

mannose $\cdot CH(OH)\cdot CHO$, and an acid $\cdot CH_2\cdot CO_2H$, which is an intermediate substance in the formation of saccharinic acid,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CMe(OH)\cdot CO_2H.$$

That lævulose is actually the intermediate substance was stated by Lobry de Bruyn to be borne out by the fact that in the action of alkalis on mannose the rotatory power becomes negative and then rises to zero owing to the increase in the amount of dextrose (*Rec. trav. chim.*, 1895, **14**, 221).*

Wohl (*Ber.*, 1900, **33**, 3093) considers that dextrose, lævulose, and mannose in alkaline solution produce a common enolic substance, $\cdot CH(OH)\cdot C(OH){:}CH(OH)\cdot$. The change of these sugars into their intermediate substance proceeds at different rates, and since it is accompanied by secondary transformations no strict equilibrium can be expected. The formation of other ketoses such as glutose might be ascribed to lævulose possessing a second enolic form, for example, $\cdot C(OH){:}C(OH)\cdot CH_2\cdot OH$.

In the review on the work on "Dynamic Isomerism," by Lowry (*British Assoc. Reports*, 1904), dextrose is stated to exist in four isodynamic modifications, of which the stereoisomeric α and β (hydrogen) glucosides are the dominant forms, the aldehyde the minor constituent, and the enolic form is present only in traces. Owing to the moderate proportion of aldoglucose present, equilibrium is rapidly established between α- and β-glucosides. Dextrose, lævulose, and mannose have a common enolic form, and the slow rate at which equilibrium is established between the three sugars in the presence of considerable quantities of alkali is an indication of the minute proportion of the enolic form in the mixture. The relationships between the three sugars allowing the existence of no less than 10 isomeric forms may be shown as follows :

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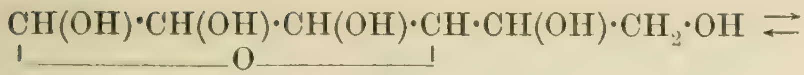
* We have not noticed such a change in the rotation angle, and we consider that Lobry de Bruyn's observations are due to the high temperature coefficient of the rotation angle of lævulose and do not represent the formation of more dextrose.



$\underbrace{\mathrm{CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH}}_{\mathrm{O}}\mathrm{\cdot CH(OH)\cdot CH_2\cdot OH} \rightleftarrows$

α- and β-glucoside
α- and β-mannoside

$\mathrm{CHO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2OH} \rightleftarrows$

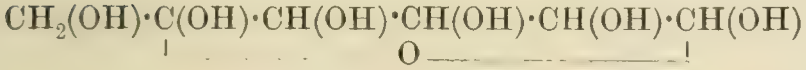
aldodextrose
aldomannose

$\mathrm{CH(OH)\colon C(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH} \rightleftarrows$

enolic form dextrose, mannose, and lævulose

$\mathrm{CH_2(OH)\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH} \rightleftarrows$

ketolævulose



$\mathrm{CH_2(OH)\cdot}\underbrace{\mathrm{C(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)}}_{\mathrm{O}}$

α- and β-fructoside

It is evident that the latter view is merely a modification of Wohl's suggestion on the lines of the generally accepted view of the structure of glucosides.

To investigate the velocity of a reaction in which the existence of at least ten isomeric forms is to be considered is not a very hopeful task. A sugar solution in the presence of an alkali might involve the consideration of all the ten forms, but in the decomposition of a solid compound of a sugar with an alkali one would be led to suppose the presence initially of only one form in preponderating quantity.

The influence of alkalis on the birotation of dextrose was shown by Trey to be a very rapidly acting one (*Zeitsch. physikal. Chem.*, 1895, **18**, 193; and 1896, **22**, 424), the normal value $[\alpha]_D$ $+52°$ being attained in fifteen minutes by addition of 0·2 gram of caustic soda to a 2·25 per cent. solution of dextrose anhydride; in sixty-five days the $[\alpha]_D$ had fallen off to $+0·44°$. Osaka (*loc. cit.*, 1901, **35**, 661) has shown that the drop in angle is strictly proportional to the concentration of the hydroxyl ions and is a reaction of the first order, the constant of which at 20° is 0·0104. Moreover, the proportionality is so close that the dissociation constants of weak bases can be determined.

Osaka obtained his velocity constant by using the expression:

$$K=\frac{1}{t}\log\frac{a_0-a_\infty}{a_t-a_\infty}$$

From Trey's numbers no attempt was made to establish a relationship between the values for rotation powers after the ordinary birotation had stopped. The change was slow and the products were probably many.

In the action of water on dextrose-, lævulose-, and mannose-guanidine, the change is slow at the ordinary temperature, but at 37° the rate is conveniently rapid, and in about six hours a constant angle is obtained. The conclusion that can be drawn from the values of the rotatory powers is that a satisfactory constant can be obtained, the value of which is given by the expression:

$$K_1 + K_2 = \frac{1}{t} \log \frac{[\alpha]_0^D - [\alpha]_\infty^D}{[\alpha]_t^D - [\alpha]_\infty^D}.$$

Dextrose Guanidine.

Experiment 1.—$t = 37°$. $c = 5·445$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	+26·54°	—
10	24·33	0·00367
20	22·31	0·00366
30	20·38	0·00371
40	18·36	0·00387
50	17·00	0·00374
60	15·51	0·00375
85	12·12	0·00384
100	10·62	0·00380
120	8·72	0·00384
∞	−0·72	Mean 0·00376

Experiment 2.—$t = 37\tfrac{1}{4}$. $c = 6·115$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	+31·96°	—
10	28·78	0·00447
20	26·00	0·00439
30	23·46	0·00438
40	21·42	0·00425
50	19·37	0·00416
60	17·74	0·00416
80	14·47	0·00419
100	11·85	0·00418
120	9·64	0·00419
150	7·03	0·00421
180	5·07	0·00423
∞	−0·57	Mean 0·00425

Experiment 3.—At room temperature. $C = 6·426$.

Mins.	$[\alpha]_D$.		$k_1 + k_2$.
0	+28·91°		—
1635	16·34		0·000126
2730	10·13		0·000131
4500	4·04		0·000134
5700	0·0		0·000157
6780	−1·55		0·000161
∞	−4·20	Mean ……	0·000142

Experiment 3.—A six days' old preparation. A little ammonia was added to the alcoholic solution of dextrose, in order to establish equilibrium between the α- and β- isomerides before guanidine was added, and the precipitate was left overnight in contact with alcohol before it was filtered off.

The initial value of the specific rotation varies with the age of the sample. When freshly prepared the $[\alpha]_D$ of dextrose guanidine is +33·52° at 37°; two months afterwards a solution of the same sample showed a specific rotation of 26·54°. The value of the velocity constant is independent of the age of the preparation.

Lævulose Guanidine.

Experiment 1.—$t = 36\frac{1}{2}°$. $c = 6·263$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	−41·35°	—
10	38·32	0·00337
30	33·21	0·00324
44	28·42	0·00378
82	21·40	0·00357
105	17·64	0·00362
166	12·21	0·00330
212	7·98	0·00352
∞	0·72	Mean 0·00349

Experiment 2.—$t = 37°$. $c = 6·3735$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	−23·85°	—
10	21·81	0·00401
20	20·29	0·00363
30	18·61	0·00372
40	17·08	0·00376
50	15·72	0·00376
60	14·51	0·00373
80	12·16	0·00382
100	10·43	0·00377
120	8·94	0·00376
140	7·92	0·00362
—	0·72	Mean 0·00376

Experiment 3.—At room temperature. $C = 6·033$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	−50·62°	—
980	43·93	0·000069
5250	15·41	0·000118
5680	13·92	0·000120
6780	11·6	0·000118
7140	10·4	0·000123
8125	7·79	0·000135
∞	4·34	Mean .. ... 0·000120

The lævulose guanidine used in Experiment 3 was precipitated from its ethyl alcohol solution by means of ether.

The initial value of the specific rotation of lævulose guanidine varies with the age of the sample. When freshly prepared the $[\alpha]_D$ is −50·62°. The value of the velocity constant is independent of the age of the preparation.

Mannose Guanidine.

Experiment 1.—$t = 37·25°$. $c = 6·9292$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	+10·03°	
60	6·38	0·00360
120	4·40	0·00336
180	3·03	0·00336
240	2·16	0·00337
300	1·44	0·00366
∞	−0·72	Mean 0·00347

Experiment 2.—$t = 37·25°$. $c = 10·391$.

Mins.	$[\alpha]_D$.	$k_1 + k_2$.
0	+8·81°	—
10	7·99	0·00391
20	7·27	0·00383
30	6·69	0·00364
40	6·16	0·00354
60	5·24	0·00339
80	4·38	0·00339
100	3·75	0·00329
120	3·32	0·00310
150	2·41	0·00322
∞	−0·72	Mean 0·00348

It will be seen that the values of the constants for dextrose-, lævulose- and mannose-guanidine are equal at the same temperature. The variation of a degree in temperature exercises a marked influence on the value of the constant.

At 34·25° the mean value of the velocity constant for dextrose guanidine was 0·00296; at 38° it was 0·00501.

At 36·5° the value of the velocity constant for lævulose guanidine was 0·00349; at 34·25° it was 0·00286.

The reason that the value of k_1+k_2 in the case of mannose is equal to the corresponding values of k_1+k_2 for lævulose- and dextrose-guanidine respectively will be explained later.

The value of $[\alpha]_D^{\infty}$ is taken to be the same in all cases, since the actually observed values for dextrose guanidine were: $[\alpha]_D^{37·5°}$ $-0·986°$; $[\alpha]_D^{17°}$ $-4·97°$; $[\alpha]_D^{15°}$ $-4·32°$; lævulose guanidine, $[\alpha]^{37·5°}$ $-1·6°$; $[\alpha]_D^{37·5°}$ $-1·77°$; $[\alpha]_D^{17°}$ $-4·34°$; mannose guanidine, $[\alpha]_D^{37·5°}$ $-0·652°$; $[\alpha]^{37·5°}$ $-0·72°$; $[\alpha]_D^{9°}$ $-3·69°$; $[\alpha]_D^{9°}$ $-3·55°$.

The final specific rotation at the ordinary temperature is nearly $-4·3°$. The lævulose guanidine shows too high a lævorotatory value, but it must be remembered with small rotation angles an error of 0·02° makes a difference of 0·2° in the value of the $[\alpha]_D$.

At the ordinary temperature the velocity of transformation (compare Experiment 3) is much slower. More than 150 hours were required before equilibrium was established in the case of dextrose- and lævulose-guanidine. The time limit at the ordinary temperature was only roughly determined, since the presence of lævulose introduces a relatively large temperature coefficient.

For the experiments at room temperature the values of k_1+k_2 are as good as can be expected, since it is difficult to maintain a constant temperature of 17—18° during the summer, when these experiments were performed; and the agreement between the $[\alpha]_D^{\infty}$ values is satisfactory. There is not the least difficulty in observing the equilibrium rotation of the guanidine sugar solutions. They change colour very slowly and show only a pale yellow colour even after being heated for ten hours at 40°; moreover, the solutions remain perfectly clear. In the presence of caustic alkalis sugar solutions darken rapidly, and in a few hours become almost opaque.

The action of methyl alcohol on lævulose guanidine is apparently similar to that of water. The initial specific rotation was $[\alpha]_D$ $-29·73°$, at the ordinary temperature falling to $[\alpha]_D$ $-4·31°$ in one hundred and forty-eight hours.

In order to examine the chemical changes which occurred during the mutarotation, aqueous solutions of guanidine sugar compounds were warmed to 40° until the equilibrium angle was reached. The products of the reaction were then investigated, following the directions given by Lobry de Bruyn (*Rev. trav. chim.*, 1895, **14**, 205).

Dextrose guanidine was found to yield 4·26 per cent. of mannose, identified by its hydrazone, and lævulose, identified by the resorcinol test; moreover, a lime compound was isolated, from which a strongly lævorotatory sugar solution was obtained, possessing the properties of lævulose.

The presence of unchanged dextrose was proved by the isolation of acid potassium saccharate:

0·1619 gave 0·0576 K_2SO_4. K = 15·95.
$C_6H_9O_8K$ requires K = 15·72 per cent.

The difficulty of removing guanidine salts rendered fermentation experiments, to test for the presence of ψ-lævulose, inconclusive.

Lævulose guanidine dissolved in water was found to give 6·1 per cent. of mannose and dextrose, identified by isolation and analysis of potassium hydrogen saccharate:

0·1475 gave 0·0515 K_2SO_4. K = 15·65.
$C_6H_9O_8K$ requires K = 15·72 per cent.

The investigation of the products of the action of water on mannose guanidine was not attempted. It is evident that they would be the same as were obtained by Lobry de Bruyn from the action of alkalis on mannose, but the amount of mannose remaining, when the equilibrium angle was reached, was determined, and this was found to be 33·8 per cent.

Lobry de Bruyn showed that, in addition to sugars, acids were formed, corresponding to a disappearance of 60 per cent. of alkali, when alkaline solutions of dextrose, lævulose, and mannose were heated to 100°. These may be saccharinic, acetic, formic, and lactic acids (H. Shade, *Zeitsch. physikal. Chem.*, 1906, **57**, 46). It was necessary to prove that the formation of these acids did not interfere with the constant determined by the change in optical angle, because saccharinic acid yields a sodium salt having $[\alpha]_D$ $-17·2°$ (Scheibler, *Ber.*, 1880, **13**, 2212).

Very small values for the velocity of disappearance of guanidine were obtained by titrating the solutions with $N/10$ hydrochloric acid, at definite intervals of time, using phenolphthalein or litmus as indicator.*

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* From the strength of guanidine as a base, it is permissible to use phenolphthalein for the purpose.

Dextrose guanidine. $t=37·25°$.
$c=5·0258$.

Mins.	$[\alpha]_D^{37\frac{1}{4}^\circ}$.	C.c. N/10-HCl.	$K=1/t \log x_0/x_t$.
0	+33·52°	27·2	—
60	19·49	26·8	0·000172
120	11·34	26·2	0·000135
180	6·57	25·8	0·000127
240	3·97	25·0	0·000152
300	2·28	23·8	0·000193
390	+0·99	21·6	Mean 0·000156
∞	+0·99	9·7	—

∞ $[\alpha]_D^{11^\circ} = -3·77°$.
x_0 = c.c. N/10-HCl used at t_0.
x_t = ,, ,, t

Laevulose guanidine. $t=36·5°$.
$c=4·278$.

Mins.	$[\alpha]_D^{36\frac{1}{2}^\circ}$.	C.c. N/10-HCl.	$K=1/t \log x_0/x_t$
0	−47·80°	33·7	—
60	32·37	32·1	0·000352
120	22·08	30·8	0·000325
180	15·42	30·4	0·000248
270	8·99	28·4	0·000275
360	5·96	27·55	0·000243
480	3·42	25·85	0·000240
600	—	24·05	0·000244
1440	—	13·45	0·000277
		Mean	0·000275

The action will be unimolecular if saccharinic acid,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CMe(OH)\cdot CO_2H$$

(Lippmann, *Chemie der Zuckerarten*, 1904, 335), or an acid,

$$CMe(OH)\cdot CO\cdot CH_2\cdot CH(OH)\cdot CO_2H,$$

be formed. The formation of lactic acid from glucose has been represented by Wohl and other authors by the following scheme:

$$CHO\cdot[CH(OH)]_4\cdot CH_2\cdot OH \longrightarrow$$
$$CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot CHMe(OH) \longrightarrow CHMe(OH)\cdot CO_2H$$

(*loc. cit.*, 1890). The production of acetaldehyde and formic acid from dextrose is represented by Schade (*Zeitsch. physikal. Chem.*, 1906, **57**, 30) by supposing that an intermediate substance,

$$CHO\cdot CH_2\cdot CH(OH)\cdot CO\cdot CH_2\cdot CHO,$$

is first formed, and this by the action of hydrogen and hydroxyl ions furnishes molecules of formic acid and acetaldehyde.*

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* Buchner, Meisenheimer, and Schade (*Ber.*, 1906, **39**, 4217) state that the conclusions arrived at by Schade can no longer be maintained. The yield of formic acid is greater and, in addition, glycollic acid and trihydroxybutyric acid are formed. The authors consider that glyceraldehyde is first formed; this under normal conditions would be transformed into methylglyoxal and so into lactic acid. The "acetaldehyde" appears to have been furfuraldehyde and is produced in very small quantity.

Mannose guanidine. $t = 37·25°$. $c = 6·9292$.

Mins.	$[\alpha]_D^{37\frac{1}{4}°}$.	C.c. $N/10$-HCl.	$K = 1/t \log x_0/x_t$.
0	+10·03°	35·3	—
60	6·38	34·8	0·000132
120	4·40	34·4	0·000093
180	3·03	33·4	0·000133
240	2·16	33·05	0·000119
300	1·23	32·7	0·000111
*420 at 37¼	0·53	29·8	0·000175
540 ,,	0·36	27·1	(0·000212)
*$[\alpha]_D^{12}$ =	−2·88	—	—
780	−0·72	23·2	(0·000233)
1020	−0·72	16·4	(0·000326)
$[\alpha]_D^{11°}$ =	−3·96	—	Mean... 0·000127

* Overnight at the ordinary temperature.

It is to be noticed that the value of the velocity constant for the disappearance of alkali is so small that it will not interfere with the value of the constant obtained from the rotation angle. It is evident that the constant obtained by Rimbach (*Zeitsch. physikal. Chem.*, 1905, **51**, 473) from the change in the rotation angle, on the assumption that only sodium saccharinate is formed by the action of caustic soda on dextrose, is not in agreement with the above numbers. He stated that the change could be represented by the equation

$$C_6H_{12}O_6 + NaOH = C_6H_{11}O_6Na + H_2O.$$

The equation was then bimolecular if in $K = \left(\frac{1}{A - x} - \frac{1}{A - x_0}\right)\frac{1}{t - t_0}$ (x = grams of dextrose transformed) t_0 and x_0 are taken ten to thirty minutes after mixing the solutions of alkali and sugar. This selection of the initial times and corresponding values of x_0 seems unnecessary; for example, at 20° thirty minutes after the commencement of the reaction, at 25° ten minutes, at 30° thirty minutes, and at 40° fifteen minutes are taken as the initial times. An explanation is possible if it is assumed that a compound of caustic soda and dextrose is first formed. The $[\alpha]_D$ of dextrose in sodium glucosate in water is 42·5°, whilst 42·5° is the $[\alpha]_D$ of the mixture of caustic soda and dextrose after thirty minutes given in Rimbach and Weber's paper. The amount of sodium saccharinate obtainable from 1 gram of dextrose was taken at 1·123 grams and its $[\alpha]_D$ − 17·2° (*loc. cit.*, 481). The constants obtained, 0·00389 at 20°, 0·01902 at 30°, are much higher than the constants obtained by us from optical measurements. Rimbach and Weber worked with stronger alkaline solutions than ours, but their experimental data will give a satisfactory constant if calculated on the formula adopted by us.

Saccharinic acid is undoubtedly a product, but lactic and other acids ought not to be left out of consideration.

Further evidence in support of these small velocity constants for the disappearance of alkali will be brought forward in considering the results of the investigation of the compounds of dextrose, lævulose, and mannose with caustic potash and soda.

It was found that when the rotation had reached a constant value the alkalinity continued to decrease until at length it became zero, but several days elapsed before the solution lost its alkalinity. The percentages of free guanidine present at optical equilibrium are for the dextrose, lævulose, and mannose compounds, 11·2 and 10·9, 12·3, 10·1 respectively, having fallen from 17·9; but these numbers are really much too low, as the alkalinity at 37·25° falls only 10—12 per cent. of its value during the first five hours, and in our experiments the solutions were kept after the first five hours at the ordinary temperature overnight, and the optical angle determined next day. It will be shown in the case of the compounds of dextrose and lævulose with caustic alkalis that the loss in alkalinity during five hours at 37·25° is about 15 per cent. of its original value. From the values of the constants calculated on the supposition that a six-carbon-atom acid is formed, it is found that the sugars yield more than one acid, or that saccharinic acid is not the sole product of the change. Moreover, when the alkaline solutions have become neutral a quarter to one-third of the sugar has disappeared, whereas for the production of a six-carbon-atom acid two-thirds ought to have disappeared.

The rates of formation and disappearance of mannose were studied separately. In one series of experiments it was found that 4—6 per cent. of mannose was formed when optical equilibrium had been attained by aqueous solutions of dextrose- and lævulose-guanidine.

In another series of experiments the changes in optical activity, the amounts of mannose hydrazone produced, as well as the weights of phenylglucosazone precipitated after the removal of mannose hydrazone, were determined in one and the same solution of mannose guanidine.

Hours.	$[\alpha]_D^{37·5}$.	Mannose found from hydrazone.	Mannose calculated.	Constant for disappearance of mannose $K = 1/t \log \frac{M_0 - M_\infty}{M_t - M_\infty}$.	Per cent. osazone on original weight of sugar present.	Per cent. G + F calculated on the assumption that 1 gram osazone = 1·12 grams mixed sugars.
0	+10·03°	100	—	—	—	—
1	6·38	89·3	85·3	0·000865	12·12	16·32
2	4·40	76·5	77·4	0·000103	18·28	23·46
3	3·03	70·24	71·9	0·000907	24·70	33·64
4	2·16	67·3	68·4	0·000764	32·71	44·53
5	1·23	65·3	64·7	0·000752	35·21	47·85
*7	−0·72	50·9	56·8	0·000848	49·17	66·94
*13	0·72	33·8	—	Mean 0·000861	55·12	75·05
23½	0·63	15·17	—		33·62	51·35
69	0·63	8·56	—		26·14	35·60

* Overnight at the ordinary temperature.

M_o, M_t, M_∞ = quantities of mannose present at t_o, t, and t_∞ respectively.

It has been pointed out by Neuberg that the presence of salts of nitrogen bases retards the formation of osazones, but guanidine salts do not prevent the complete precipitation of mannose hydrazone, as may be shown by the following experiment. 0·2144 Gram of guanidine carbonate was dissolved in a 3·153 per cent. aqueous solution of mannose. On treatment with phenylhydrazine acetate at 0°, 0·9407 gram of mannose hydrazone was obtained. Percentage of mannose hydrazone precipitated = 99·4.

These numbers show that as the mannose decreases the amount of osazone increases up to a maximum and then diminishes; the percentages of dextrose and lævulose are only very approximately accurate, because they are calculated on the assumption that 1 gram of osazone = 1·12 grams of sugar; moreover, the influence of guanidine in the precipitation of the osazone may be appreciable, nevertheless the errors will be of a constant nature and will not interfere with the order of the change. The phenylglucosazone precipitated, after having been washed with ether, decomposed at 199° instead of 205°, so that it was not quite pure.

It is remarkable that when dextrose and lævulose reach optical equilibrium 5 per cent. of mannose is present, but when mannose has reached optical equilibrium only 50 per cent. of the mannose has been transformed.

The velocity constant for the disappearance of mannose, on the assumption that 5 per cent. is the true value of concentration of the mannose when the change is complete, is much smaller than that obtained from the rotation values of dextrose, lævulose, and mannose, and yet the rate of change in rotation angle for mannose is the same as for the two preceding sugars. We have endeavoured to explain this by the following hypothesis:

It has been shown that if $k_1 + k_2 = \frac{1}{t} \log \frac{A_o^D - A_\infty^D}{A_t^D - A_\infty^D}$, then $k_1 + k_2 = 0{\cdot}0036$ for dextrose- and lævulose-guanidine respectively.

The equilibrium constant $K = \frac{k_2}{k_1}$ is equal to the ratio of the masses of dextrose and lævulose in equilibrium. Expressing this in terms of the specific optical rotations:

$$K = \frac{k_2}{k_1} = \frac{\text{specific rotation of lævulose guanidine} - \text{constant } [\alpha]^D}{\text{constant } [\alpha]_D - [\alpha]_D \text{ of dextrose guanidine}} = \frac{-48{\cdot}54^\circ - (-0{\cdot}72^\circ)}{-0{\cdot}72^\circ - 32{\cdot}15^\circ} = 1{\cdot}45$$

(Hudson, *Zeitsch. physikal. Chem.*, 1903, **44**, 491).

Since $k_1 + k_2 = 0{\cdot}0036$

$k_2 = 0{\cdot}0021. \qquad k_1 = 0{\cdot}0015.$

Therefore the velocity constant $G \longrightarrow F = k_1 = 0{\cdot}0015$ and the velocity constant $F \longrightarrow G = k_2 = 0{\cdot}0021$.

In obtaining the value of these constants, the formation of any mannose has not been taken into account, because that sugar cannot be detected in solutions of dextrose- and lævulose guanidine, nor in dextrose- and lævulose-soda solutions until the optical equilibrium has been nearly reached. It will be shown later that at the constant specific rotation 58 per cent. of dextrose and 42 per cent. of lævulose are present in the solution. From these numbers and the value of $k_1 + k_2 = 0{\cdot}0036$, it follows that $k_1 = 0{\cdot}0015$ and $k_2 = 0{\cdot}0021$, since if A_1 = amount of dextrose at the beginning of the experiment, A_2 that of lævulose in the reverse reaction, and x gram molecules of dextrose be transformed after time t into lævulose:

$$\frac{dx_1}{dt} = k_1(A_1 - x) \qquad \frac{dx_2}{dt} = k_2(A_2 + x).$$

At equilibrium:

$$\frac{dx}{dt} = k_1(A_1 - x) - k_2(A_2 + x) = 0$$

$$\frac{k_1}{k_2} = \frac{A_2 + x}{A_1 - x}$$

Suppose 100 per cent. of dextrose present at the commencement of the experiment, at equilibrium 58 per cent. would be present and 42 per cent. transformed; therefore:

$$x = 42$$

$$\frac{k_1}{k_2} = \frac{0 + 42}{100 - 42} = \frac{42}{58}$$

$k_1 + k_2 = 0{\cdot}0036$.
$k_1 = 0{\cdot}0015$ and $k_2 = 0{\cdot}0021$.

It is possible to calculate what will be the amount of mannose present at any time t during the change which the mannose guanidine undergoes in aqueous solution. It must be assumed that the transformation of dextrose, lævulose, and mannose may be represented by the following scheme:

$$\begin{tikzcd}
 & D \arrow[dr, leftrightarrow, dashed] & \\
M \arrow[ur] \arrow[dr] & & X \\
 & L \arrow[ur, leftrightarrow, dashed] &
\end{tikzcd}$$

X = an intermediate substance the concentration of which at any time is negligible (Jungius, *Zeitsch. physikal. Chem.*, 1905, **52**, 99).

If mannose guanidine be transformed at any moment into lævulose- and dextrose-guanidine in the proportions of 0·0021 and 0·0015, since the values of the $[\alpha]_D$ of lævulose- and dextrose-guanidine are respectively $-48{\cdot}54^\circ$ and $+32{\cdot}15^\circ$, the $[\alpha]_D$ of the mixture would be $-14{\cdot}9^\circ$. Because $\frac{21}{36} \times -48{\cdot}54 - \frac{15}{36} \times 32{\cdot}15 = -14{\cdot}9^\circ$ must be the rotation angle of the mixture of dextrose and lævulose formed from mannose. Consequently, at every moment the mannose guanidine $[\alpha]_D$ $+10{\cdot}03°$ is being transformed into a mixture with $[\alpha]_D$ $-14{\cdot}9°$. After one hour the $[\alpha]_D$ was found to be $+6{\cdot}38°$; therefore the percentage of mannose remaining at that time is:

$$\frac{6{\cdot}38 - (-14{\cdot}9) \times 100}{10{\cdot}03 - (-14{\cdot}9)} = 85{\cdot}3.$$

It is assumed that the fall in the angle is proportional to the amount of mannose transformed.

The calculated values agree very fairly with the experimental percentages of mannose obtained from its hydrazone (see p. 1024). Special precautions were taken in the estimation of the hydrazones. Bourquelot and Hérissey's directions (*Compt. rend.*, 1899, **129**, 339) were followed as to the quantities to be used, and in every case the hydrazone was precipitated at 0°, and kept at that temperature for two hours before it was filtered off. It was found that no osazone was precipitated under these conditions, and the presence of lævulose did not interfere with the estimation. The hydrazone was collected on a weighed filter paper, washed with cold water and ether, and dried at 100°:

0·4955 mannose gave 0·7305 hydrazone, mannose = 98·28 per cent.

0·7275 ,, mixed with 0·3272 lævulose gave 1·0785 hydrazone, mannose = 98·9 per cent.

0·4045 mannose mixed with 1·2985 lævulose gave 0·6005 hydrazone, mannose = 98·1 per cent.

The agreement in the results is well within the experimental error of the determination.

At first it was thought that the passage of mannose into dextrose could be represented by the scheme:

$$\begin{tikzcd} & & D \\ M \arrow[r, shift left] & X \arrow[l, shift left] \arrow[ur, leftrightarrow] \arrow[dr, leftrightarrow] & \\ & & L \end{tikzcd}$$

When dextrose and lævulose are in equilibrium, the specific rotation of the mixture is $-1°$, and the proportions of the two sugars are nearly 58 : 42. The value of $k_1 + k_2$, obtained from the change in the rotation angle of mannose guanidine, is 0·0036, and the value of k_1, obtained from the weights of mannose hydrazone, is 0·00086. Therefore the value of $k_2 = 0{\cdot}00274$, and this represents the velocity constant of the change $X \longrightarrow M$; but as mannose cannot be detected in guanidine-dextrose and -lævulose solutions until equilibrium in optical activity has been established, it follows that $X \longrightarrow M$ must have an extremely small velocity. The scheme thus described is not in keeping with the experimental facts.

Another representation would be that put forward by Lobry de Bruyn, namely:

$$M \rightleftarrows L \rightleftarrows D.$$

If this were so, starting with mannose guanidine it would be expected that the lævulose would always be in slight excess until the equilibrium between lævulose and dextrose had been established. From results obtained from an investigation of mannose-soda, it would appear that lævulose is always in excess until after the equilibrium angle is reached. As the mannose continues to disappear, the dextrose increases until 5 per cent. of mannose is left, together with 51·5 per cent. of dextrose and 43·5 per cent. of lævulose. It must be noticed that these are the quantities of the three sugars present when optical equilibrium has been reached in the case of dextrose- and lævulose-guanidine.

In the representation described on p. 1026,

$$\begin{tikzcd}
 & L \arrow[dr, leftrightarrow] & \\
M \arrow[ur, leftrightarrow] \arrow[dr, leftrightarrow] & & X \\
 & D \arrow[ur, leftrightarrow] &
\end{tikzcd}$$

it is assumed that mannose gives rise to a mixture of lævulose and dextrose, the former being in the predominant quantity. The $[\alpha]_D$ of the mixture is $-14·9°$, and it contains 58 per cent. of lævulose and 42 per cent. of dextrose. If mannose passes to both lævulose and dextrose, the proportions of lævulose and dextrose will be by Wegscheider's test for side reactions independent of the time and constant. From experiments with solutions of mannose-soda it has been found that the ratio of fructose and glucose formed is 54 : 46 up to the tenth hour of the change. On the assumption of such a side reaction the quantities of mannose present in solutions of mannose-soda have been calculated with fair accuracy. The equality of the velocity constants of the guanidine compound of the three sugars can be explained by considering the final equilibrium angle ($-0·72°$) and the angles observed from time to time. Actually the mannose passes with a velocity constant of 0·00086 into a mixture of dextrose and lævulose with a calculated $[\alpha]_D$ $-14·8°$. This mixture passes into an equilibrium mixture $[\alpha]_D$ $-0·72°$ with a more rapid velocity. At every moment of the change, lævulose and dextrose, in the proportions of 58 to 42, are being formed, and this mixture then passes to an equilibrium mixture $[\alpha]_D$ $-0·72°$ of lævulose and dextrose in the proportions of 42 : 58. At every moment, from one part of mannose, 0·0005 part of lævulose and 0·00036 part of dextrose are being formed. These change into an equilibrium mixture of 0·0005 part of dextrose and 0·00036 part of lævulose, so that while 58 parts of lævulose are formed at the same time as 42 parts dextrose, the 58 parts of lævulose pass to 58 parts dextrose in the same time that 42 parts dextrose furnish 42 of lævulose. The reason why the $[\alpha]_D$ $-0{\cdot}72°$ is reached while 50—51 per cent. of mannose is present is that the remaining mannose guanidine, with $[\alpha]_D$ $10{\cdot}03 \times 0{\cdot}57 = 5{\cdot}7$, is in contact with a mixture with an $[\alpha]_D$ of $-14{\cdot}9 \times 0{\cdot}43 = -6{\cdot}4$; therefore the total $[\alpha]_D$ is $-0{\cdot}7°$, that is, the equilibrium $[\alpha]_D$. The change of mannose into lævulose and dextrose continues, but cannot be followed by the polarimeter.

Mannose passes to lævulose and dextrose, and these attain an equilibrium mixture with $[\alpha]_D$ $-0{\cdot}72°$. Actually the change followed optically is equivalent to

M ⟶ equilibrium mixture of dextrose and lævulose $[\alpha]_D$ $-0{\cdot}72°$.

Such a change would be represented by $K_1 = \frac{1}{t}\log\frac{a_0 - a_\infty}{a_t - a_\infty}$ and the constant would be the same as in the case of lævulose and dextrose.

In the later stages of the change disturbing factors are more marked; the intermediate substance *X*, the concentration of which may be considered small, owing to its relatively rapid change into dextrose and lævulose, furnishes acids at the expense of the sugars. There would seem to be a limit at which *X* yields dextrose or lævulose; when this is reached *X* continues to give rise to acids, causing a disappearance of the sugars until the hydroxyl ions disappear and the reaction stops. It will be shown in a later communication that from the determination of the reducing power of alkaline sugar solutions after optical equilibrium is reached the alkalinity goes on decreasing, and the dextrose and lævulose disappear, but the ratio of the amounts of dextrose to lævulose remains constant. Moreover, it has been shown that the yield of glucosazone after reaching a maximum diminishes, and in the case of mannose guanidine the sugar decreases uniformly until 8 per cent. of it is left.

An attempt was made to determine the velocity of change of the reducing power during the mutarotation of dextrose guanidine. Owing to the presence of the nitrogenous base, Pavy's method was alone available. The modification described by Peska (*Chem. Zeit. Rep.*, 1895, 257) was employed. The lævulose formed was destroyed by treatment with hydrochloric acid according to Sieben's method (*Zeitsch. anal. Chem.*, 1885, **24**, 137). During the estimation a difficulty was encountered owing to the presence of the guanidine: on warming the Pavy's solution to 80° and adding the sugar solution, a turbidity appeared which made the disappearance of the blue colour of the solution rather difficult to detect. Nevertheless very fairly concordant results were obtained. The following table shows the values obtained:

(*a*) One hundred c.c. of Pavy's solution required 20·3 c.c. of a 4 per cent. dextrose solution. Therefore 100 c.c. Pavy's solution = 0·0802 gram dextrose.

(*b*) One hundred c.c. of Pavy's solution required 22·5 c.c. of a 4 per cent. lævulose solution. Therefore 100 c.c. Pavy's solution = 0·09 gram lævulose.

(*c*) One hundred c.c. of Pavy's solution was titrated with 20 c.c. of a 5·0258 per cent. solution of dextrose guanidine diluted to 200 c.c.

(*d*) Ten c.c. of a 5·0258 per cent. solution of dextrose guanidine were heated for three hours to 100° with 6 *N*-hydrochloric acid according to the directions given by Muller (*Chem. Zeit.*, 1888, 12, 240). After neutralisation the volume was made up to 100 c.c., and 100 c.c. of Pavy's solution were used for the titration.

Hours.	$[\alpha]_D^{37\cdot5}$.	*c.* c.c. dextrose guanidine solution required for 100 c.c. Pavy's solution 20·2 c.c. were found to contain 0·0802 gram dextrose, calc. = 0·0830 or 0·410 gram in 100 c.c.	*d.* c.c. after boiling with HCl, required for 100 c.c. of Pavy's solution.	F : G = (*d* − *c*) : *c*.	Per cent. lævulose in mixture of dextrose and lævulose.
0	+33·52°	20·2	21·0	0·039	3·7
1	19·49	20·4	24·5	0·20	16·7
2	11·34	20·8	27·8	0·336	25·2
3	6·57	21·2	32·1	0·514	34
4	3·97	21·4	34·55	0·64	41
5	2·28	21·7	36·3	0·67	40
6	0·99	21·8	38·4	0·76	43
13*	0·99	26·7	42·5	0·59	37

* And 35 hours at the ordinary temperature.

A similar experiment was performed with lævulose guanidine.

(*a*) Twenty c.c. of a 4·275 per cent. solution of lævulose guanidine were diluted to 200 c.c., and 100 c.c. of Pavy's solution were used for the titration.

(*b*) Ten c.c. of a 4·275 per cent. solution were heated for three hours with 6 *N*-hydrochloric acid, neutralised, and made up to 100 c.c., and 100 c.c. of Pavy's solution were used for the titration.

Hours.	$[\alpha]_D^{36}$.	*a.* c.c. lævulose guanidine solution required for 100 c.c. of Pavy's solution.	*b.* c.c. after boiling with HCl, required for 100 c.c. of Pavy's solution.	F : G = (*b* − *a*) : *a*.	Per cent. lævulose in mixture of dextrose and lævulose present.
0	−47·80°	24·0	—	—	—
1	32·37	24·0	96·6	3·0	75
2	22·08	24·05	60·2	1·5	60
3	15·42	24·2	53·2	1·17	54
4½	8·99	24·75	49·2	0·98	49
6	5·96	25·0	47·75	0·91	47
8	3·42	25·35	47·0	0·85	46
10	—	26·4	46·75	0·77	43
24	—	29·15	48·75	0·67	40

In spite of the difference of the reducing powers of dextrose and lævulose, the numbers in column *a* have been taken as proportional to the amounts of lævulose and dextrose respectively. The difference is not great and will affect the percentages of lævulose only slightly, especially when the unavoidable experimental errors in the values in column *b* are considered.

The reducing power of the solutions does not change appreciably, and the small increase in the number of c.c. may be accounted for by the inferior reducing powers of the acids which are slowly produced.

In the case of dextrose guanidine, after the sixth hour, the ratio of dextrose to lævulose, or ketohexose, remains constant, or nearly so, and although the dextrose is disappearing, the lævulose is disappearing at the same rate. In the case of lævulose guanidine, the experiment was performed at a somewhat lower temperature; for example, 36° instead of 37·25°; consequently the velocity of transformation was slower, and it was not until the tenth hour that the ratio of dextrose to lævulose became constant. This constancy of the ratio of dextrose to lævulose when optical equilibrium has been obtained has been confirmed in the action of water on dextrose-soda and lævulose-soda.

The calculated proportions of dextrose and lævulose present when $[\alpha]_D = -1°$ are 58 per cent. and 42 per cent. respectively; the proportions found experimentally, 57—60 and 40—43 per cent. respectively, are in very fair agreement with these numbers.

The conclusions to be drawn from the mutarotation of solutions of dextrose-, lævulose-, and mannose-guanidine are:

(1) The fall in angle to a constant minimum represents in the case of dextrose- and lævulose-guanidine an apparent equilibrium between dextrose and lævulose through an intermediate substance X, the concentration of which at any moment is very small:

$$D \longleftrightarrow X \longleftrightarrow L.$$

(2) The fall in angle to a constant minimum in the case of mannose guanidine represents the formation of lævulose and dextrose according to the scheme:

$$\begin{tikzcd} & D \arrow[dr, leftrightarrow] & \\ M \arrow[ur] \arrow[dr] & & X \\ & L \arrow[ur, leftrightarrow] & \end{tikzcd}$$

(3) The velocity constant for the transformation of dextrose to lævulose $= 0·0015$.

The velocity constant for the transformation of lævulose to dextrose $= 0·0021$.

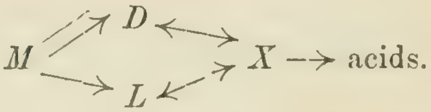
The velocity constant for the transformation of mannose to lævulose and dextrose $= 0·00086$.

The velocity constant for the transformation of mannose to lævulose $=0{\cdot}0005$.

The velocity constant for the transformation of mannose to dextrose $=0{\cdot}00036$.

The velocity of the reverse change of lævulose and dextrose into mannose is very small. (The velocity constants were determined at 37°.)

(4) There is a continual slow disappearance of X to form acids, accompanied by disappearance of dextrose and lævulose in constant proportion, and by the disappearance of mannose according to the scheme:



(5) The velocity constant for the disappearance of alkali in lævulose guanidine $=0{\cdot}000275$.

The velocity constant for the disappearance of alkali in dextrose guanidine $=0{\cdot}000156$.

The velocity constant for the disappearance of alkali in mannose guanidine $=0{\cdot}000127$.

The difference in the first two velocity constants is too large; probably it may be due to experimental errors, but if the concentration of X at any moment is not always negligibly small, part of X may change to acids instead of to a sugar.

These conclusions are similar in substance to those put forward by Wohl from the study of the results of the chemical changes observed by Lobry de Bruyn.

In our investigations attempts have been made to follow the course of the chemical changes by quantitative methods, and to avail ourselves of as many independent methods as we could use to determine the values of the constants involved.

We wish to thank Professor Liveing and Professor Sir James Dewar for permission to carry out part of this work in the University Laboratory.

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XCVII.—*Esterification Constants of Substituted Acrylic Acids. Part II.*

By John Joseph Sudborough and Ebenezer Rees Thomas.

In Part I (Sudborough and Roberts, Trans., 1905, 87, 1840) attention was drawn to the difference observed between the esterification constant of an unsaturated acid and that of its saturated analogue. The values obtained were as follows:

Unsaturated.	$E^{15°}_{MeOH}$.	Saturated	$E^{15°}_{MeOH}$.
Crotonic acid	1·28	Butyric acid	41·63
Cinnamic acid	0·937	β-Phenylpropionic acid	43·20
Methyl hydrogen fumarate	1·79	Methyl hydrogen succinate	17·25
Methyl hydrogen maleate	0·859		

The unsaturated acids examined were all of the αβ-type, namely, substituted acrylic acids. We deemed it advisable to extend the investigation by the inclusion of unsaturated olefine acids in which the double linking was not in the αβ-position. The present paper gives an account of the determination of the constants for the following acids: cinnamic; phenyl*iso*crotonic, $CHPh⁚CH·CH_2·CO_2H$; β-ethylacrylic acid, $CH_3·CH_2·CH⁚CH·CO_2H$; ethylidenepropionic,

$CH_3·CH⁚CH·CH_2·CO_2H$,

and allylacetic, $CH_2⁚CH·CH_2·CH_2·CO_2H$.

The results were all obtained with the same sample of Kahlbaum's No. 1 methyl alcohol, which was distilled over lime and over sodium; the results are thus comparable; they cannot, however, be compared with the constants previously obtained for other acids (Trans., 1904, 85, 534, and 1905, 87, 1840), as this specimen of alcohol gave values much below those obtained for other samples of Kahlbaum's methyl alcohol. Determinations made with cinnamic acid and β-phenylpropionic acid show that the constants given in this paper would have to be practically doubled to be comparable with those given previously.

The values obtained for the acids at 15° were:

Cinnamic acid	0·481
β-Ethylacrylic acid	0·746
Allylacetic acid	19·94
Phenyl*iso*crotonic acid	35·5
Ethylidenepropionic acid	37·1

The values at once indicate the effect produced by the position of the double linking on the rate of esterification. In the αβ-position the double bond has a considerable retarding effect, whereas its influence in the $\beta\gamma$- or γ-position is comparatively small and the esterification constants of such unsaturated acids are of much the same order of magnitude as the constants for the corresponding saturated acids.

It is intended to extend the investigation by an examination of the rates of esterification of other unsaturated acids in order to see whether the generalisation indicated above holds good in all cases.

EXPERIMENTAL.

The method adopted in each case was exactly similar to that already described (Trans., 1905, **87**, 1841).

Cinnamic Acid, m. p. 133—133·5°.

A.—Strength of the hydrochloric acid before mixing = 0·0894*N*.

15 c.c. of the cinnamic acid solution required 15·40 c.c. of 0·1*N*-baryta solution.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
2	14·87	0·00760
4	14·20	0·00880
6	13·54	0·00931
8	12·98	0·00928

Mean of last three = 0·00913.

B.—Strength of the hydrochloric acid before mixing = 0·0833*N*.

15 c.c. of the cinnamic acid solution required 16·06 c.c. of 0·10*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
2	15·30	0·01052
4	14·80	0·00887
6	14·23	0·00876
8	13·58	0·00910

Mean of last three = 0·00891.

Calculated for 0·05*N*-hydrochloric acid *A* = 0·0102 ; *B* = 0·0107. Mean = 0·01045.

Constant = 0·01045 × 20 × 2·3026.
= 0·481.

*Phenyl*isocrotonic *Acid*, $CHPh{:}CH{\cdot}CH_2{\cdot}CO_2H$.

This acid was prepared by the method described by Jayne (*Annalen*, 1883, **216**, 97). Phenylparaconic acid was synthesised by heating a mixture of benzaldehyde, sodium succinate, and acetic anhydride at 100—110°, a temperature somewhat lower than recommended by Jayne. To prepare the unsaturated acid it was found advisable to heat the paraconic acid, which had been previously dried at 100°, in a flask until the evolution of carbon dioxide had practically ceased and then to distil under reduced pressure. The distillate was treated with sodium carbonate solution, the alkaline solution extracted with ether to remove small amounts of neutral products and acidified with hydrochloric acid. The precipitated acid was dried and recrystallised from carbon disulphide, when it melted at 86°.

A.—Strength of the hydrochloric acid before mixing = 0·0416*N*.

15 c.c. of the alcoholic solution required 31·4 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
0·5	20·80	0·358
1	14·98	0·321
1·5	10·50	0·317
2	7·24	0·319

Mean of last three = 0·319.

B.—Strength of the hydrochloric acid before mixing = 0·0207*N*.

15 c.c. of the alcoholic solution required 30·96 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
0·5	25·48	0·169
1	21·60	0·156
1·5	17·82	0·160
2	15·06	0·156

Mean = 0·160.

Calculated for 0·05*N*-hydrochloric acid $A=0·767$; $B=0·773$. Mean = 0·770.

$$\text{Constant} = 0·770 \times 20 \times 2·3026.$$
$$= 35·5.$$

Allylacetic Acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$,

This acid was prepared by Fittig and Messerschmidt's method (*Annalen*, 1881, **208**, 92) by the hydrolysis of ethyl allylacetoacetate. Some considerable care is required in carrying out the hydrolysis. The ester is added gradually, the mixture well shaken, and afterwards carefully heated. If the heating is carried out too rapidly a dark coloration is produced and the yield of allylacetic acid is poor. The boiling point is 187—189° under atmospheric pressure.

A.—Strength of the hydrochloric acid before mixing = 0·0207*N*.

15 c.c. of the alcoholic solution required 32·98 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
0·5	29·46	0·0980
1	26·60	0·0934
1·5	24·32	0·0882
2	22·00	0·0879

Mean of last three = 0·0898.

B.—Strength of the hydrochloric acid before mixing = 0·0207*N*.

15 c.c. of the alcoholic solution required 31·26 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
1	25·06	0·0960
2	20·58	0·0908
2·75	17·72	0·0896
3·5	15·38	0·0880

Mean of last three = 0·0895.

Corrected for 0·05*N*-hydrochloric acid = 0·433.

$$\text{Constant} = 0·433 \times 20 \times 2·3026.$$
$$= 19·94.$$

β-Ethylacrylic Acid.

The isomeric β-ethylacrylic and ethylidenepropionic acids were prepared and separated by Fittig and Mackenzie's method (*Annalen*, 1894, **283**, 83). From 50 grams of malonic acid 16 grams of the mixed acids were obtained (F. and M., 12·5) when the temperature was gradually raised and some 110 hours taken for the completion of the reaction. The separation of the two acids by Fittig and Mackenzie's method is tedious and but poor yields are obtained. It is possible that the separation could be more readily accomplished by making use of the different rates at which the two acids are esterified. The β-ethylacrylic acid distilled at 199—202° and solidified when cooled slightly below 0°; a small amount of liquid was removed by filter paper and the residual solid melted at about +7°. (F. and M. give 9·5—10·5° as the melting point of the pure acid.)

A.—Strength of the hydrochloric acid before mixing = 0·0833*N*.

15 c.c. of the alcoholic solution required 27·90 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
2	25·60	0·0187
4·5	24·16	0·0139
6	23·14	0·0136
7	22·74	0·0127

Mean of last three = 0·0134.

B.—Strength of the hydrochloric acid before mixing = 0·0833*N*.

15 c.c. of the alcoholic solution required 27·28 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
2	25·08	0·0183
4	23·86	0·0145
6	22·64	0·0135
8·5	21·20	0·0129

Mean of last three = 0·0136.

Calculated mean for 0·05*N*-hydrochloric acid = 0·0162.

$$\text{Constant} = 0·0162 \times 20 \times 2·3026.$$
$$= 0·746.$$

Ethylidenepropionic Acid.

The barium salt which is insoluble in alcohol was crystallised from water and decomposed by hydrochloric acid. The acid distilled at 192—193·5° under atmospheric pressure.

A.—Strength of the hydrochloric acid before mixing = 0·0416*N*.

15 c.c. of the alcoholic solution required 29·16 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
1	13·06	0·349
1·25	10·90	0·342
1·5	9·12	0·337
1·75	7·74	0·329

Mean = 0·339.

B.—Strength of the hydrochloric acid before mixing = 0·0207*N*.

15 c.c. of the alcoholic solution required 27·88 c.c. of 0·05*N*-baryta.

t (in hours).	$a-x$.	$1/t\log_{10}a/a-x$.
0·5	23·22	0·159
1	18·84	0·170
1·5	15·68	0·167
2	13·12	0·164

Mean = 0·165.

Calculated for 0·05*N*-hydrochloric acid $A = 0·815$; $B = 0·797$. Mean = 0·806.

$$\text{Constant} = 0·806 \times 20 \times 2·3026.$$
$$= 37·1.$$

The cost of this investigation has been partly met by a grant from the Royal Society, for which we desire to express our thanks.

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XCVIII.—*The Addition of Iodine to Acetylenic Acids.*

By THOMAS CAMPBELL JAMES and JOHN JOSEPH SUDBOROUGH.

THE addition of iodine to acetylene derivatives has been previously investigated by Liebermann and Sachse (*Ber.*, 1891, **24**, 4112), Bruck (*ibid.*, 4118; 1893, **26**, 843), and Peratoner (*Gazzetta*, 1892, **22**, [ii], 77). Liebermann and Sachse obtained good yields of the di-iodides of phenylpropiolic, stearolic, and behenolic acids by dissolving the acids in carbon disulphide and adding the theoretical amount of iodine and some calcium iodide (some 10 per cent. of the acid used). After ten days practically all the acid was converted into the di-iodide. These same chemists also proved that the di-iodides are formed when the acid is heated for an hour or so with calcium iodide and the theoretical amount of iodine at temperatures varying from 100—150°. Bruck proved that propargylic acid, tetrolic acid, and acetylenedicarboxylic acid combine with iodine when their chloroform or alcoholic solutions are heated with iodine in sealed tubes at 100°. Peratoner studied the addition of iodine to acetylene hydrocarbons and found that di-iodides are formed when the hydrocarbon and iodine are dissolved in a suitable solvent (for example, carbon disulphide or alcohol) and the mixture kept for some months at the ordinary temperature or for several hours at 100°.

As we were desirous of obtaining appreciable quantities of $\alpha\beta$-di-iodocinnamic acid we undertook the investigation of the addition of iodine to phenylpropiolic acid and other acetylenic acids with the hope of finding a simpler and quicker method for bringing about the addition. As aqueous solutions are the most convenient to work with we used the potassium salts of the acids and liberated nascent iodine in the presence of a solution of the salt; the iodine was liberated by the action of cupric sulphate solution on potassium iodide. Very good yields of $\alpha\beta$-di-iodocinnamic acid and $\alpha\beta$-di-iodocrotonic acid were obtained from phenylpropiolic and tetrolic acids respectively. The acid is readily isolated when the solution is warmed, the insoluble cuprous iodide removed, and the filtrate acidified. Small amounts remain in solution and may be extracted by ether.

We have also been able to prove that the same di-iodides may be obtained by mixing a solution of the potassium salt of the acid with an excess of iodine in potassium iodide solution and leaving for some three to five days. The acid may be isolated by acidifying the solution, filtering, and washing the precipitate with potassium iodide solution in order to remove free iodine.

Attempts have been made to isolate di-iodides from *o*- and *p*-nitrophenylpropiolic acids and from acetylenedicarboxylic acid by both methods at the ordinary temperature. The numbers given in Tables III and IV indicate that both the *o*- and *p*-nitro-acids combine with iodine, although not so readily as phenylpropiolic acids, Table I. The inability to isolate a di-iodide in the two cases appears to be due to the instability of these compounds. Yellow products have been obtained, but immediately these are filtered iodine is liberated and when washed with potassium iodide or thiosulphate all the iodine is given up and the original acids are obtained.

In the case of acetylenedicarboxylic acid there is no doubt but that there is not the same tendency for this acid to combine with iodine as is met with in most acetylenic acids (compare Bruck, *loc. cit.*, 4118). No additive compound could be isolated and when the mixture of iodine in potassium iodide solution and potassium acetylenedicarboxylate was titrated in order to determine the velocity constant of the reaction, the results proved that no addition had taken place within one hundred and sixty-one hours (Table V). This is interesting, as it is in agreement with the results obtained by Hugo Bauer (*Ber.*, 1904, **37**, 3317) on the addition of bromine to ethylene derivatives and also with the results obtained by J. Thomas and one of us on the same subject. Experiments made by J. Thomas on the addition of bromine to olefinic acids clearly indicate that a carboxylic group has a powerful inhibiting action on the addition of bromine to an olefine compound. Unsaturated acids with the double bond in the $\alpha\beta$-position combine with bromine very slowly in the dark, whereas olefinic acids with the double bond in any other position combine with the greatest readiness.

We have not been able to obtain additive compounds of olefinic acids and iodine by either of the two methods described above. In all cases the original acids were obtained. The acids tried were crotonic, cinnamic, and glutaconic, together with sorbic acid, cinnamylideneacetic acid, and phenylcinnamylideneacetic acid,

$$\mathrm{CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CO_2H},$$

which contain conjugated double bonds. In many cases an insoluble copper salt of the original acid was precipitated on the addition of the cupric sulphate solution.

The velocity constants of the reactions, potassium tetrolate and iodine, potassium phenylpropiolate and iodine, potassium *o*-nitrophenylpropiolate and iodine, and potassium *p*-nitrophenylpropiolate and iodine, have been determined in aqueous solution at 15° in the presence of potassium iodide, and the results in each case indicate that the reaction is bimolecular.

A comparison of the velocity constants of potassium phenylpropiolate and potassium tetrolate in aqueous solution (Tables I and II) show that the acid containing the methyl radicle adds on iodine less readily than the acid containing the phenyl group in the corresponding position. These results are analogous to the results obtained by Sudborough and Thomas (Proc., 1906, 22, 318) for the addition of bromine to crotonic and cinnamic acids in carbon tetrachloride solution and also to those obtained by Barrett and Lapworth on the same acids in aqueous solution.

The velocity constant of the reaction between phenylpropiolic acid and iodine in absolute alcoholic solution has been determined (Table VI) and the results show that the reaction is much slower than in the aqueous solution. When the same reaction is tried in absolute alcohol previously saturated with potassium iodide the velocity is reduced to practically nil (Table VI).

The following sets of experiments were conducted in 70 per cent. alcoholic solution.

(*a*) Phenylpropiolic acid and iodine in presence of potassium iodide, Table VII.

(*b*) The same, but without potassium iodide, Table VIII.

(*c*) Potassium phenylpropiolate and iodine in presence of potassium iodide, Table VII.

(*d*) The same without potassium iodide, Table VIII.

The results show that the acid and its potassium salt combine with iodine at practically the same rate in the absence of potassium iodide and that the introduction of potassium iodide reduces the velocity constant considerably in both cases.

The reactions in 70 per cent. alcohol and in the absence of potassium iodide (Table VIII) do not appear to be bimolecular. When the ordinary equation for a bimolecular reaction is used the values for K are not constant, but diminish considerably as t increases. This may be due to side-reactions.

An experiment was made in order to determine whether the reaction between phenylpropiolic acid and iodine is reversible in alcoholic solution. The results (Expt. 12) indicate that at 15° the reaction

$$C_6H_5\cdot C{\vdots}C\cdot CO_2H + I_2 \rightleftarrows C_6H_5\cdot CI{:}CI\cdot CO_2H$$

is reversible, but the reverse reaction takes place extremely slowly.

Some of the results obtained by us are interesting when compared with results obtained by Barrett and Lapworth (Proc., 1907, 23, 18). Their data indicate that in very dilute aqueous solution cinnamic acid combines with bromine more readily than does crotonic acid. In the case of benzylidenemalonic acid the addition of bromine in aqueous solution takes place more readily with the sodium salt than with the free acid. The addition of potassium bromide lowers the velocity of the reaction to an appreciable extent.

EXPERIMENTAL.

αβ-Di-iodocinnamic Acid.

Expt. 1.—2·1 Grams of phenylpropiolic acid were dissolved in a solution of 1 gram of potassium carbonate in 20 c.c. of water, 12 grams of potassium iodide were added, and then a solution of 7·2 grams of hydrated cupric sulphate in 30 c.c. of water run in from a dropping funnel whilst the mixture was kept well stirred. At the beginning the liberated iodine appeared to be absorbed immediately, but towards the end free iodine was always present. After remaining at the ordinary temperature for an hour the mixture was warmed and filtered in order to remove cuprous iodide. The clear filtrate was acidified with an excess of hydrochloric acid, kept for a short time, and the precipitated di-iodo-acid filtered, washed with potassium iodide solution and then with water. 4·75 Grams of dry di-iodide were obtained, and on extracting the filtrate with ether a further 0·2 gram, making a total of 4·95 grams or an 88 per cent. yield. The acid after recrystallisation from chloroform melted at 172°. Liebermann and Sachse (*loc. cit.*) give 171°.

Expt. 2.—2·92 Grams of phenylpropiolic acid were treated in the same manner as in Expt. 1, except that the mixture was warmed immediately after the cupric sulphate solution had been run in and then filtered. The precipitated acid weighed 5·6 grams, which is equal to a 70 per cent. yield.

Expt. 3.—0·55 Gram of phenylpropiolic acid was dissolved in 10 c.c. of water containing 0·26 gram of potassium carbonate and the solution mixed with a solution of 2 grams of iodine and 3 grams of potassium iodide in 50 c.c. of water. The mixture was allowed to stand in bright sunlight and a heavy precipitate appeared in the course of several hours. At the end of three days the mixture was precipitated with dilute hydrochloric acid, filtered, washed with potassium iodide solution, then with water, and dried. A theoretical yield of 1·5 grams of αβ-di-iodocinnamic acid was obtained; the melting point of the crude product was 155—160°, but after one crystallisation was raised to 172°.

Expt. 4.—This was similar to No. 3, but the mixture was placed in a dark cupboard. A precipitate appeared at the end of two days. The mixture was kept in the dark for a week and was then acidified and treated as before. A theoretical yield of 1·5 grams of the compound, melting at 167—168°, was obtained, and after recrystallisation the melting point was 172°.

Expt. 5.—Similar to No. 3, but 2·2 grams of phenylpropiolic acid were used, together with 1·03 grams of potassium carbonate, 5 grams of iodine, 5 grams of potassium iodide, and 50 c.c. of water. A precipitate appeared after twenty-four hours and continued to increase for two or three days. After three days the solution was acidified and treated in the usual manner. Yield, 5·5 grams = 95 per cent.

αβ-Di-iodocrotonic Acid, $CH_3{\cdot}CI{:}CI{\cdot}CO_2H$.

Expt. 6.—1·2 Grams of tetrolic acid and 1 gram of potassium carbonate were dissolved in 10 c.c. of water, the solution mixed with a solution of 12 grams of potassium iodide in 10 c.c. of water, and to this mixture a solution of 7·2 grams of hydrated cupric sulphate in 30 c.c. of water was gradually added. The mixture was then treated in exactly the same manner as in the isolation of di-iodocinnamic acid in Expt. 1. The precipitated acid weighed 3·8 grams, and the acid obtained by extracting the filtrate with ether 0·9 gram; this gives a total of 4·7 grams, which is equivalent to a 98 per cent. yield. The melting point of the product was 125°.

Expt. 7.—A similar experiment to No. 6 was made, but was conducted in the dark and at 0°. After the mixture had been kept overnight, the di-iodo-acid, melting at 125°, was precipitated. Yield, 2·1 grams.

Expt. 8.—0·6 Gram of tetrolic acid was dissolved in the theoretical amount of potassium carbonate solution (25 c.c.) and mixed with a solution of 4 grams of iodine and 4 grams of potassium iodide in 25 c.c. of water. The mixture was placed in sunlight, but no precipitate appeared. After five days the solution was acidified and treated in the usual manner. Two grams of *αβ*-di-iodocrotonic acid, melting at 118—120°, were obtained. Yield = 83 per cent. After crystallisation from carbon disulphide the melting point was raised to 125°.

Expt. 9.—Similar to No. 8, except that 5·2 grams of tetrolic acid were used. Yield of di-iodide, 15 grams = 89 per cent.

o-*Nitrophenylpropiolic Acid and Iodine.*

Expt. 10.—0·7 Gram of acid and 0·25 gram of potassium carbonate were dissolved in 10 c.c. of water, mixed with 2 grams of iodine and 3 grams of potassium iodide dissolved in 10 c.c. of water, and the mixture placed in sunlight for several days. On acidifying, a yellow precipitate appeared, which rapidly turned dark. As it was difficult to separate the precipitate by filtration, the whole was extracted with ether, the ethereal extract washed with dilute thiosulphate solution, dried, and evaporated. 0·7 Gram of unaltered acid, free from halogen and melting at 150—151°, was obtained.

p-*Nitrophenylpropiolic Acid and Iodine.*

Expt. 11.—0·96 Gram of acid was treated in the same manner as described in No. 10. No precipitate appeared during the course of a fortnight. The ethereal extract, after washing with sulphurous acid, gave the unaltered acid.

Experiments with Olefine Acids.

Experiments with nascent iodine obtained by the copper sulphate method were made in connexion with crotonic, cinnamic, glutaconic, sorbic, cinnamylideneacetic, and cinnamylidenephenylacetic acids. In each case the original acid was obtained by precipitation or by extraction with ether. Cinnamic acid and the two last-named acids gave insoluble copper salts.

Experiments were also made with acrylic, crotonic, and sorbic acids by the iodine and potassium iodide method, but the original acids were recovered after acidification, extraction with ether, and washing the ethereal solution with thiosulphate.

Velocity Constants.

In dealing with the reactions in aqueous solutions the general method has been to mix 100 c.c. of a 0·2 *N*-solution * of the potassium salt with an equal volume of 0·2 *N*-iodine solution in potassium iodide in a brown bottle, to keep this in a thermostat at 15°, and to titrate 25 c.c. of the mixture with 0·1 *N*-sodium thiosulphate solution after given intervals of time.

In all the tables given the times are taken in hours and the concentrations represented in c.c.'s of thiosulphate. The constants in all the tables are comparable, as the same concentrations, same temperature, same volumes of mixture, and same concentration of thiosulphate were used throughout.

TABLE I.—*Potassium Phenylpropiolate.*

A.—$a=24·96$.				*B.*—$a=24·96$.			
t.	$a-x$.	x.	$1/t.x/a(a-x)$.	t.	$a-x$.	x.	$1/t.x/a(a-x)$.
2	21·95	3·01	$2·75 \times 10^{-3}$	20	10·39	14·57	$2·81 \times 10^{-3}$
6	17·86	7·10	2·65 ,,	24	9·25	15·71	2·83 ,,
10	15·14	9·82	2·60 ,,	28	8·45	16·51	2·80 ,,
				42	6·36	18·60	2·79 ,,

Mean of the two sets $=2·75 \times 10^{-3}$.

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* A solution containing 0·1 gram-mol. per litre.

Table II.—*Potassium Tetrolate.*

A.—$a = 25·0$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$.
5	22·75	2·25	7·91 × 10^{-4}
24·5	16·78	8·22	8·00 ,,
*29·5	15·24	9·76	8·69 ,,

B.—$a = 25·0$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$.
4	23·20	1·80	7·76 × 10^{-4}
25	16·77	8·23	7·86 ,,
50	12·50	12·50	8·00 ,,
71	10·57	14·43	7·69 ,,
76	10·15	14·85	7·71 ,,

Mean of seven numbers = 7·85 × 10^{-4}.

* Temperature rose to 15·5°.

Table III.—*Potassium* o-*Nitrophenylpropiolate.*

A.—$a = 25$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$.
3	23·70	1·30	7·31 × 10^{-4}
8	21·98	3·02	6·87 ,,
24	17·92	7·08	6·59 ,,
46	14·79	10·21	6·00 ,,

B.—$a = 25$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$
21·5	18·86	6·14	6·06 × 10^{-4}
48	14·68	10·32	5·86 ,,

Mean of *A* and *B* = 6·45 × 10^{-4}.

Table IV.—*Potassium* p-*Nitrophenylpropiolate.*

$a = 25$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$.
3·2	23·87	1·13	5·92 × 10^{-4}
17·5	20·50	4·50	5·02 ,,
24	19·44	5·56	4·77 ,,
28	18·69	6·31	4·82 ,,
42	16·81	8·19	4·64 ,,
66	14·50	10·50	4·39 ,,

Mean = 4·93 × 10^{-4}.

Table V.—*Potassium Acetylenedicarboxylate.*

$a = 24·96$.

t	3	17	65	161
$a - x$	24·85	24·90	24·85	24·84

Table VI.—*Phenylpropiolic Acid in* 99·8 *per cent. Ethyl Alcohol.*

One hundred c.c. of a solution containing 1·460 grams of the acid were mixed with 100 c.c. of an 0·2 *N*-solution of iodine in absolute alcohol and placed in the thermostat at 15°. Twenty-five c.c. of the mixture were used for titration with 0·1 *N*-thiosulphate.

$a = 25·07$.

t.	$a - x$.	x.	$1/t.x/a(a-x)$.
4	24·86	0·21	8·42 × 10^{-5}
25	24·00	1·07	7·12 ,,
52	23·46	1·61	5·27 ,,
76	22·78	2·29	5·28 ,,
148	20·75	4·32	5·61 ,,

A similar experiment was made, but the solution was saturated with potassium iodide.

$a = 25·56.$

t	20	68	140
a − *x*................	25·56	25·56	25·46

Table VII.—Two sets of experiments were made with 70 per cent. alcohol in the presence of potassium iodide. The quantities were similar to those in Table VI. Set *A* refers to the free acid and set *B* to the potassium salt.

A.—Acid. $a = 25·0$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
24	24·9	0·1	$6·69 \times 10^{-6}$
48	24·8	0·2	6·72 ,,
168	24·4	0·6	5·86 ,,

B.—Potassium salt. $a = 25·08$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
24	24·98	0·1	$6·65 \times 10^{-6}$
168	24·4	0·68	6·62 ,,
528	23·14	1·94	6·33 ,,

Table VIII.—Similar experiments were made with the acid and potassium salt in 70 per cent. alcohol, but without the addition of potassium iodide. Sets *A* and *B* refer to the free acid and sets *C* and *D* to the potassium salt.

A.—$a = 25$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
24	18·49	6·51	$5·87 \times 10^{-4}$
48	15·92	9·08	4·75 ,,
72	14·36	10·64	4·12 ,,
120	12·19	12·81	3·51 ,,
164	11·57	13·43	2·83 ,,

B.—$a = 25$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
24	18·03	6·97	$6·44 \times 10^{-4}$
48	15·47	9·53	5·13 ,,
76	13·83	11·17	4·25 ,,
171	10·99	14·01	2·99 ,,
316	10·45	14·55	1·76 ,,

C.—$a = 25$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
24	14·75	10·25	$11·58 \times 10^{-4}$
44	13·53	11·47	7·71 ,,
48	13·22	11·78	7·43 ,,
67	12·60	12·40	5·87 ,,
96	12·11	12·89	4·44 ,,

D.—$a = 25$.

t.	*a* − *x*.	*x*.	$1/t.x/a(a-x)$.
25	13·70	11·30	$13·20 \times 10^{-4}$
48	12·24	12·76	8·69 ,,
72	11·51	13·49	6·51 ,,
168	10·48	14·42	3·28 ,,
312	9·54	15·46	2·08 ,,
500	8·81	16·19	1·47 ,,

Exp. 12.—Two grams of pure di-iodocinnamic acid were dissolved in 100 c.c. of 70 per cent. ethyl alcohol in a brown bottle and kept at 15°.

After forty days, 25 c.c. of the solution required 0·75 c.c. of 0·1 *N*-thiosulphate to react with the liberated iodine.

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XCIX.—*Mercury Derivatives of Pseudo-Acids containing the Group* ·CO·NH·.

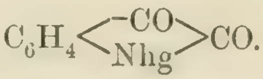
By S. J. MANSON AULD, Ph.D.

SINCE the discovery of the two structural isomeric mercuric salts of cyanuric acid by Hantzsch (*Ber.*, 1902, **35**, 2717), the study of the mercury derivatives of other pseudo-acids has appeared of special interest. Thus, although the tautomeric compound $C_3H_3O_3N_3$ does not exist in the forms $(CO)_3(NH)_3$ and $(CN)_3(OH)_3$, yet the corresponding mercury derivatives $(CN)_3(Ohg)_3$ and $(CO)_3(Nhg)_3$ have been isolated, and it would therefore appear that mercury derivatives are more capable of existence in isomeric forms than the hydrogen compounds.

At Professor Hantzsch's suggestion it was therefore resolved to extend this investigation to other tautomeric hydrogen compounds and particularly to pseudo-acids, to see whether structural isomeric mercury salts, or at least mercury derivatives with different attachment of the metal, could be obtained. Thus, if O:X·H represents the pseudo-acid and X·OH the true acid, the mercury salts O:X·hg and X·Ohg are possible. Further, it was at least of interest to determine what constitution is actually possessed by mercury compounds existing only in one form, whether, for example, the pseudo-acids with the group ·CO·NH· give *O*- or *N*-salts.

Thanks to the work of Pesci (*Zeitsch. anorg. Chem.*, 1897, **15**, 208; 1898, **17**, 276; 1899, **21**, 361. *Gazzetta*, 1894, **24**, 449; 1898, **28**, 436; 1902, **32**, 277), Dimroth (*Ber.*, 1898, **31**, 2154; 1899, **32**, 758; 1902, **35**, 2032, 2853), and Ley (*Ber.*, 1899, **32**, 1357; 1900, **33**, 1010; 1902, **35**, 1309), this question can be decided in nearly every case, for it has been found that mercury salts with oxygen-linking (at any rate when they are soluble in water) give the ordinary ionic reactions for mercury with alkalis, potassium iodide, and hydrogen sulphide. Mercury united with carbon cannot be detected by the above means and the author's experience here and elsewhere confirms the view that nitrogen-linked mercury reacts, when at all, only with hydrogen sulphide.

Structural isomerism of the same nature as that of the mercuric cyanurates has not indeed been discovered. All the pseudo-acids examined containing the group ·CO·NH· (with the exception of cyanuric acid) form only one mercury derivative; in all cases this has been an *N*-salt with the group ·CO·Nhg. Uric acid and its alkyl derivatives, barbituric and violuric acids, benzoylcyanamide and others act in this manner, and recently Peters (*Ber.*, 1907, **40**, 235) has also shown that only one mercury derivative of isatin exists, namely, an *N*-salt of the formula



$$C_6H_4<\begin{matrix}-CO\\ Nhg\end{matrix}>CO.$$

Under certain conditions these mercury *N*-compounds react as "mercury acids" and form alkali salts. In this manner mercuriviolurie acid produces highly coloured alkali mercuriviolurates. Only when the nitrogen is completely substituted by alkyl groups are *O*-salts formed, as, for instance, by dimethylvioluric acid.

Less to be expected is the fact, already demonstrated by Ley and Kissel (*Ber.*, 1899, **32**, 1357), that the nitroamines (nitrourethane, methylnitroamine) do not give *N*-salts of the formula $R\cdot Nhg\cdot NO_2$, but always *O*-mercury salts. A definite explanation of this difference in behaviour cannot up to the present be given.

Uric Acid Derivatives.

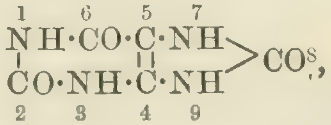
Uric acid itself does not dissolve freshly precipitated mercuric oxide in the cold, and on heating the latter is reduced. By addition of mercuric acetate to a solution of the sodium salt, however, the *mercuric* salt, $C_5H_2O_3N_4Hg$, is formed as a white, amorphous precipitate which can be obtained as a fine, white powder after washing and drying. This salt does not give mercuric oxide with sodium hydroxide solution, and is therefore to be regarded as an *N*-salt:

0·2740 gave 0·1740 HgS. Hg = 54·75.

$C_5H_2O_3N_4Hg$ requires Hg = 54·65 per cent.

3-*Methyluric acid* and 7-*methyluric acid* do not reduce mercuric oxide, but otherwise behave similarly to uric acid and therefore produce *N*-salts. 3 : 7-*Dimethyluric acid* gives an *N*-salt by double decomposition of its sodium salt with mercuric acetate, which, however, unlike those mentioned above, dissolves in caustic soda and is reprecipitated by dilute acids.

1 : 3 : 7-*Trimethyluric acid.*—A mercury salt could not be obtained from this acid under any conditions, either by the use of mercuric oxide or soluble mercuric salts. It is probable therefore that in uric acid,



$$\begin{array}{l}\overset{1}{N}H\cdot\overset{6}{C}O\cdot\overset{5}{C}\cdot\overset{7}{N}H\\ \mid\qquad\qquad\quad \Vert\\ \underset{2}{C}O\cdot\underset{3}{N}H\cdot\underset{4}{C}\cdot\underset{9}{N}H\end{array}>CO^8,$$

only the hydrogen atoms in the positions (1) and (3) are capable of substitution by the mercuric radicle.

ψ-Uric acid (*carbamidomalonylurea*), like uric acid, reduces mercuric oxide on warming. The mercuric salt, prepared in the same way, is also an *N*-salt.

0·2635 gave 0·1085 HgS. Hg = 35·48.

$C_{10}H_{10}O_8N_8Hg$ requires Hg = 35·08 per cent.

Methyluracyl gives an amorphous, alkali-stable *N*-salt both by heating with mercuric oxide and from its sodium salt with mercuric acetate.

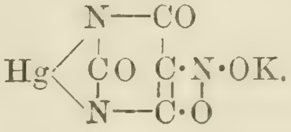
Violuric Acid.—By precipitating a solution of the sodium salt with mercuric acetate solution, violuric acid gives the mercuric salt, $C_4HO_4N_3Hg$, as an amorphous, pale flesh-coloured substance:

0·2760 gave 0·1805 HgS. Hg = 56·37.

$C_4HO_4N_3Hg$ requires Hg = 56·33 per cent.

That the mercury in it is linked direct to nitrogen is apparent from its highly characteristic behaviour towards alkalis, whereby it is transformed into intensely coloured alkali salts of "mercurivioluric acid." On treatment of the mercuric violurate with caustic potash, it is changed at once into a deep violet potassium salt. The colour of this substance changes to a lighter shade on standing and more quickly on warming, but varies from pink to pinkish-violet, even when prepared under apparently identical conditions.

These salts of different shade, when washed and air-dried and then heated for some time at 110°, lose in weight, and are all transformed into the same pale blue salt. As the loss in weight varies with the colour, the difference in shade appears to be dependent on a varying content of water. The loss in weight on heating is greater the deeper the colour of the precipitate. Thus, a pink salt lost only 6·9 per cent. of water, a violet salt, on the other hand, 10·05 per cent. of water. The pale blue salt is *potassium mercuriviolurate*,



(For the structural formula compare Guinchard, *Ber.*, 1899, **32**, 1723.)
Analysis (*a*) from pink salt:

0·1340 gave 0·0283 K_2SO_4. K = 9·48.
0·3185 „ 0·2050 HgS. Hg = 51·61.
(*b*) From violet salt:
0·7000 gave 0·1583 K_2SO_4. K = 9·80.

$C_4O_4N_3HgK$ requires K = 9·92; Hg = 50·91 per cent.

The sodium salt shows the same peculiarities as the potassium salt, but is less stable, as it loses sodium continuously on washing with water. All the alkali salts of mercurivioluric acid, both hydrated and anhydrous, regenerate mercurivioluric acid on treatment with dilute acids.

As was to be expected, *dimethylvioluric acid* behaves in a different manner. The compound, prepared from dimethylalloxan and hydroxylamine, reduces mercuric oxide on warming, but gives by double decomposition a red, crystalline *O*-salt, which shows all the mercury reactions.

Saccharin behaves in a rather curious manner. Although a fairly strong acid ($K = 0·38$), it does not attack mercuric oxide. By the precipitation method, there is formed a gelatinous compound which dissolves in excess of alkali, and is reprecipitated unchanged by passing carbon dioxide through the solution. Whether an *N*-salt has been formed or a mercurisaccharin containing mercury in the benzene nucleus could not be decided, and the matter will be investigated further.

Benzoylcyanamide is also not acted on by mercuric oxide. The white, amorphous compound obtained by double decomposition is an *N*-salt, unattacked by caustic alkali :

0·2100 gave 0·0990 HgS. Hg = 40·57.

$C_{16}H_{10}O_2N_4Hg$ requires Hg = 40·81 per cent.

Carbostyril.—In alcoholic solution, carbostyril gives immediately with mercuric acetate, more slowly with mercuric chloride, a thick, white precipitate, which is also formed on boiling carbostyril with mercuric oxide. After washing with water and alcohol, it was found to possess the empirical formula $C_{27}H_{19}O_3N_3Hg$:

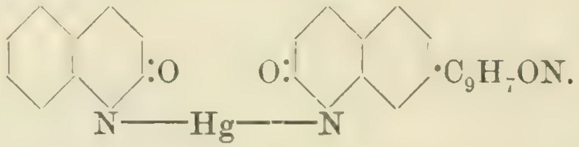
0·1872 gave 0·0680 HgS. Hg = 31·32.
0·1752 „ 0·0640 HgS. Hg = 31·49.

$C_{27}H_{19}O_3N_3Hg$ requires Hg = 31·59 per cent.

This formula is to be regarded as $(C_9H_6ON)_2Hg + C_9H_7ON$.

The substance is therefore a fairly stable double compound of one molecule of mercuricarbostyril and one molecule of carbostyril. Similar mercury double compounds have been prepared by Pesci, notably from aniline (*Zeitsch. anorg. Chem.*, 1897, 15, 212).

This compound can only be dissolved to any extent by pyridine and a mixture of acetone and chloroform. As it is not attacked by caustic soda and potassium iodide, but reacts with hydrogen sulphide, it must be a mercury *N*-compound of the formula



It dissolves in dilute acids with decomposition into carbostyril and mercuric salt. It is also soluble in warm dilute sodium hydroxide, and can be precipitated unchanged by careful acidification. As the mercury cannot be precipitated from the alkaline solution by means of hydrogen sulphide, the metal seems to have changed its functions, and at the same time its method of linking. This curious behaviour was not further investigated, it having been shown that all pseudo-acids with the group $\cdot CO\cdot NH\cdot$ give analogously constituted mercury salts of the formula $\cdot CO\cdot Nhg$.

UNIVERSITY, LEIPZIG, and
EAST LONDON COLLEGE.

C.—*The Constitution of the Diazo-compounds.*

By JOHN CANNELL CAIN.

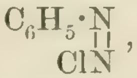
ALTHOUGH the long controversy between Hantzsch and Bamberger on this subject apparently came to an end some few years ago, and many chemists have accepted the views of the former, yet it would appear that there is still some uncertainty of opinion with regard to the constitution of these substances.

The stereochemical hypothesis of the constitution of the metallic diazo-derivatives (also cyanides, &c.), so stoutly advocated by Hantzsch, has been sharply criticised by Bamberger, von Pechmann, Blomstrand, and Armstrong, but the re-introduction of Blomstrand's formula for the diazo-salts by Bamberger in 1895 has met with hardly any opposition.

Although this formula, for example, $C_6H_5\cdot NCl\vdots N$, advocated, as it has been, by no less than three chemists independently (Blomstrand, 1869, Strecker, 1871, and Erlenmeyer, 1874), was rejected on the ground that it did not explain the formation of phenylhydrazine from diazobenzene chloride by reduction as did Kekulé's formula,

$$C_6H_5\cdot N{:}NCl,$$

it must be admitted that the reasons given by Bamberger for discarding the latter were slight. This chemist indeed only advanced the old criticism of Blomstrand that Kekulé's formula was that of a chloride of nitrogen and as such was improbable. Apparently Bamberger was not quite sure as to which of the two formulæ, $C_6H_5\cdot NCl\vdots N$ and $C_6H_5\cdot N{:}NCl$, was the more preferable, but finally chose the former. Hantzsch did not at first agree with this view; he regarded diazobenzene chloride as a *syn*-diazo-compound,



$$\begin{matrix}C_6H_5\cdot N\\ \|\\ ClN\end{matrix},$$

but soon rejected this and agreed with Bamberger in adopting the Blomstrand formula.

It is necessary to point out here that Blomstrand's formula was used, not so much that the reactions of the diazo-salts demanded it, but from the analogy with the ammonium salts, and that the Kekulé formula was required for the metallic diazo derivatives. Later, Hantzsch adduced much evidence, chiefly from the physical side, in favour of the so-called diazonium formula, from the resemblance which existed between these salts and the ammonium salts in solution. It is true, of course, that diazobenzene chloride results from aniline hydrochloride by replacement of three atoms of hydrogen, but by no means does it follow that the constitutions of the two are analogous. Moreover, the diazo-compounds are in a class entirely by themselves; their behaviour and reactions are different from those of any other series of compounds, and straining after analogous constitutions in cases like this is dangerous. The whole framework of this supposed resemblance is shaken when we remember that the commonly accepted constitution of the ammonium compounds is by no means certain and is very different from that which is probably the true one.*

In the whole of the literature bearing on the constitution of the diazo-compounds it is remarkable that, with one important exception which will be referred to presently, they are treated solely from the point of view of nitrogen derivatives: they are compared with either nitrogen chloride (argument against Kekulé's formula), with metallic salts (ammonium, potassium, &c.), or with aliphatic substituted quaternary ammonium derivatives. In no discussion of their constitution (with the above exception) is the condition of the benzene ring taken into consideration; this is tacitly assumed to remain in exactly the same condition as it was in the aniline hydrochloride before being converted into the diazo-chloride. In view of our modern ideas on the extreme mobility of the benzene nucleus it is surprising that conceptions of mobility have been practically confined to the diazo-part of the molecule. When, however, we regard such a compound as diazobenzene chloride as a substituted benzene derivative $C_6H_5(N_2Cl)$ and consider its properties in this light, we cannot but be impressed, *inter alia*, by the remarkable ease with which it loses the whole of its nitrogen. Those derivatives of benzene which contain only one atom of nitrogen in the substituting group (for example, aniline) manifest a very great resistance to parting with it. Such compounds withstand the action of almost all reagents with the singular exception of oxidising agents. Moreover, it is very often the case that when an atom or group is introduced into a nucleus with great ease, it is also readily removed ; we might therefore expect that as an atom of nitrogen is easily substituted for three atoms of hydrogen in aniline hydrochloride, this atom would be easily eliminated. There is, however, nothing to indicate in either of the formulæ, $C_6H_5{\cdot}NCl{:}N$ or $C_6H_5{\cdot}N{:}NCl$, that the union of the nitrogen atom with the benzene ring would be easily broken. It would, indeed, be reasonable to expect that only the second nitrogen atom would be readily split off by the various reagents.

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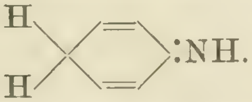
* Compare Werner, *Annalen*, 1902, **322**, 261; Cain, *Mem. Manchester Phil. Soc.*, 1904, **48**, No. 14; *Ber.*, 1905, **38**, 2715. It is, perhaps, not out of place here to point out that at the time of the inception of the ordinary ammonium theory by Ampère (1816) nitrogen was regarded as being the only element which could exhibit variable valency; the unitary formula, $H_3N{<}^{Cl}_{H}$, for ammonium chloride was therefore obvious. Had it been known, as it is now, that chlorine and oxygen could also become tervalent and quadrivalent respectively, it is highly probable that the formulæ for ammonium chloride and hydroxide respectively would have been written as I have suggested (*loc. cit.*), namely, $H_3N{:}ClH$ and $H_3N{:}OH_2$.

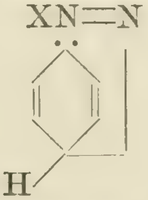
In seeking for an explanation of this fact we are driven to examine the case, already referred to, in which the nitrogen attached to the benzene ring is easily removed. This happens, of course, in the formation of *p*-benzoquinone by the oxidation of aniline. Now recent work by Ostrogowich and Silbermann (*Bull. Soc. Sci. Bucharest*, 1906, **15**, 281) has shown that there is considerable evidence in support of the view of these authors that when oxidising agents or free halogens act on amines, quinoneimides are first formed, and that the parent substance of benzoquinone is the tautomeric form of aniline,



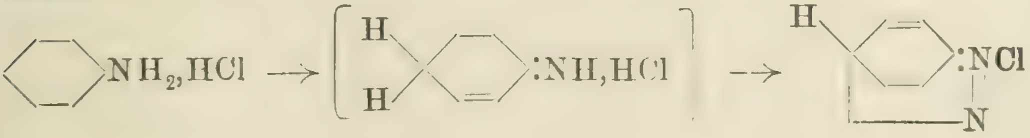
It is evident that a compound of this constitution would readily tend to split off the nitrogen at the double linking.

Now the diazotising process bears a considerable resemblance to the foregoing reaction, and it seems likely, therefore, that in this case also the tautomeric form of aniline may be the first result of the action of nitrous acid.

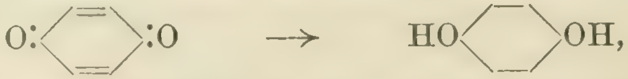
Further, it would seem necessary that any formula for the diazo-salts should contain a quinquevalent nitrogen atom, and the only formula which can satisfy the foregoing conditions is



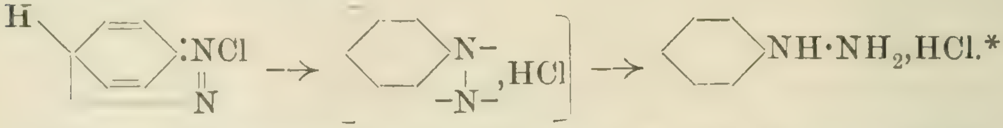
Diazobenzene chloride thus results from aniline hydrochloride as follows :



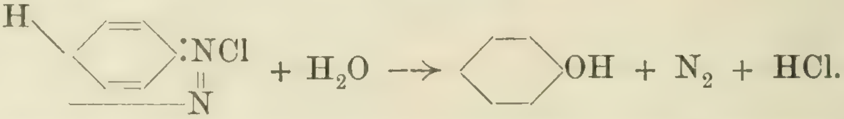
It will be seen at once that this formula readily explains those properties of diazobenzene chloride which have been already discussed. Just as benzoquinone, on reduction, loses its quinonoid configuration



so does diazobenzene chloride, in its conversion to phenylhydrazine, undergo the same change:

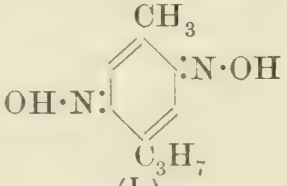


Further, the decomposition with water, as would be expected, takes place with rupture of the double linking, thus:

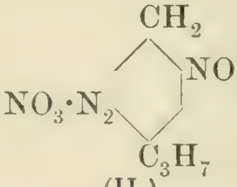


The various other decompositions are explained in the same way. It must be noted that this formula being "ring-quinonoid" or "semi-quinonoid" does not represent diazobenzene chloride as a true quinone, consequently there is no reason why, according to this formulation, this compound should be coloured, although, of course, coloured diazo-salts are well-known (compare Hantzsch, Proc., 1905, **21**, 298).

An important reaction in connexion with this constitution is the production of diazo-compounds directly from substances possessing undoubtedly the quinonoid structure. By acting on quinonedioximes with nitrogen peroxide, Oliveri-Tortorici found (*Gazzetta*, 1900, **30**, i, 526) that nitrosodiazo-compounds resulted; thus thymoquinonedioxime (I) yields the compound (II).

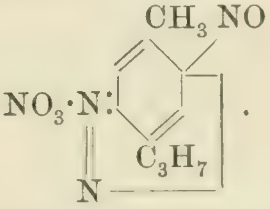


(I.)



(II.)

It is difficult to imagine why the quinonoid configuration should disappear in this reaction, and the simplest explanation of this change is offered by the formula here suggested, namely,



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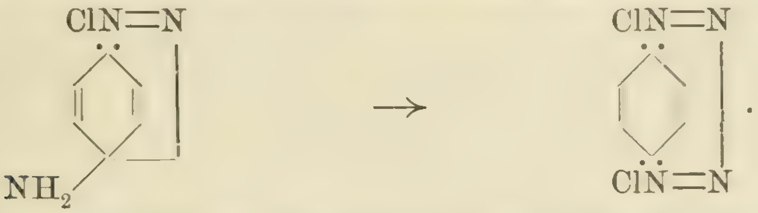
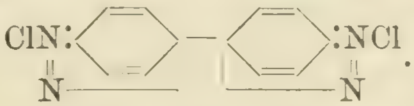
* In order to make this transformation clearer I have written phenylhydrazine hydrochloride as $C_6H_5·NH·NH_2,HCl$.

This formula also indicates why both N·OH groups are not changed into the diazo-group, for when we consider the case of *p*-phenylenediamine, which, as is well known, can only be converted into the bisdiazo-compound under special conditions, we find that the reason of this is that the linking of the second nitrogen atom with the para-carbon atom must first be broken in order to allow the second aminic nitrogen to become attached by two bonds, the final condition probably being that the second nitrogen atoms in each case are united thus:



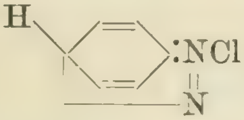
This may well explain the difference in the behaviour of *p*-phenylenediamine and diamines of the type of benzidine which are converted into the bisdiazo-compounds without difficulty, thus:



Applying this reasoning to the case of thymoquinonedioxime it is reasonable to suppose that the para-linking of the second nitrogen atom of the diazo-group cannot be broken under the conditions of the reaction.

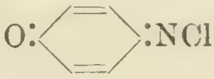
It is interesting at this point to compare the properties of diazobenzene chloride with those of, for example, quinonechloroimide, when a surprising similarity is apparent.

Diazobenzene chloride.



Readily soluble in water; decomposes by heating with water, fission taking place at the double-linked nitrogen atom. With concentrated hydrochloric acid gives chlorobenzene. Explodes on heating.*

Quinonechloroimide.



Readily soluble in hot water; decomposes by heating with water to 100°, fission taking place at the double-linked nitrogen atom.

With concentrated hydrochloric acid gives chlorophenol. Detonates above 85°.

There is, so far as I am aware, no record in the literature as to the behaviour of quinonechloroimide in solution. I am greatly indebted, therefore, to Prof. James Walker for light on this point. At Prof. Walker's request Miss H. H. Beveridge prepared a specimen of quinonechloroimide and determined its conductivity. Prof. Walker writes:

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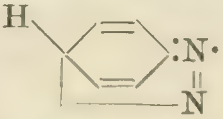
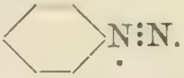
* On one occasion recorded by Hantzsch (*Ber.*, 1897, **30**, 2342), diazobenzene chloride exploded spontaneously with very great violence.

"The solution gave no precipitate with silver nitrate, indicating absence of chloridion, and had a conductivity only six times as great as that of the water employed. The solution was 0·16*N*, so that it had a conductivity only about 0·3 per cent. of a corresponding solution of an ordinary saline chloride."

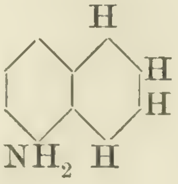
The fact that diazobenzene chloride is electrolytically dissociated in solution is thus a strong argument in favour of the presence of quinquevalent nitrogen, and there is no reason why the radicle diazonium, should not possess the constitution



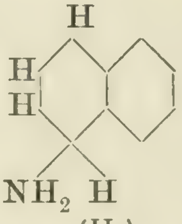
instead of



Not only does this formula explain satisfactorily the reactions of diazobenzene salts, but it throws new light on many phenomena which have hitherto been unexplained. For example, it is obvious that diazo-salts (chlorides, &c.) can only be formed from those amines which are capable of allowing the quinonoid formation to take place; thus *ar*-tetrahydronaphthylamine (I) forms diazo-salts, whilst the *ac*-compound (II) does not.

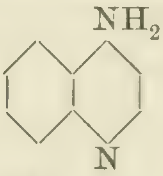


(I.)

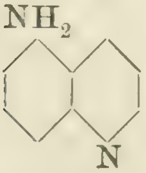


(II.)

Another example is furnished by the aminoquinolines,

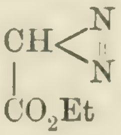


gives no diazo-salt

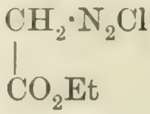


gives a crystalline diazo-chloride.

It is obvious also that one cannot expect the formation of a diazo-chloride from an aliphatic amine, as no quinonoid structure is possible, but it has hitherto remained unexplained why the diazo-compound prepared, for example, from aminoacetic ester should have the composition

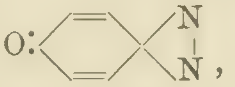


and not

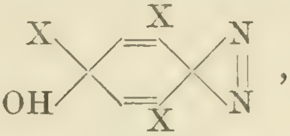


$$\begin{array}{l} CH_2{\cdot}N_2Cl \\ | \\ CO_2Et \end{array}$$

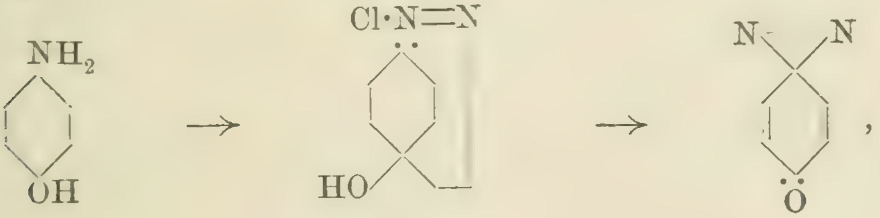
It has been indicated in the earlier portion of this paper that in one class of diazo-compounds the configuration of the benzene ring had already been taken into consideration in discussing the constitution of the diazo-nucleus. This is, of course, the class of the quinonediazides. Wolf has shown (*Annalen*, 1900, **312**, 119) that the so-called diazophenols must have the constitution



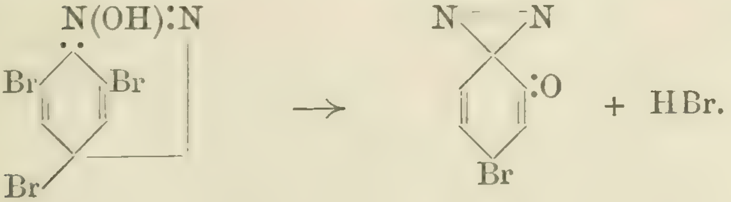
and Orton (*Proc. Roy. Soc.*, 1902, **71**, 153; Trans., 1903, **83**, 796) has shown that, in the various transformations which halogen substituted diazobenzene salts of weak acids undergo in aqueous solution, the benzene ring assumes the (ortho)quinonoid state. He even makes the interesting suggestion that such compounds when in solution may become paraquinonoid in structure, thus:



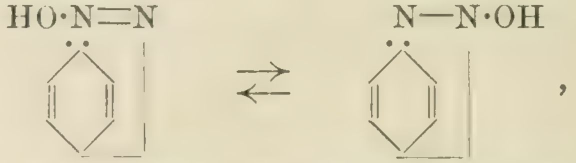
and adds that "there is a strong and increasing weight of evidence in favour of the view that in isomeric rearrangements of this type the benzene nucleus transiently assumes a quinonoid linking." These phenomena are evidently very satisfactorily explained if the first phase is of a quinonoid character; thus, in the case of the aminophenols we have



and the transformation described by Orton may be written, for example:

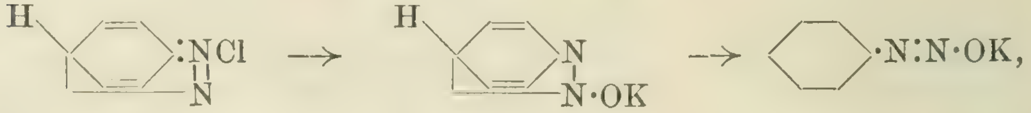


Constitution of the Metallic Diazo-compounds.—Although in the formula here suggested for the diazo-salts it may be regarded as certain that the acidic nucleus is firmly united with the quinquevalent nitrogen atom, when we investigate the case of the corresponding hydroxide it is evident that tautomerism may occur, thus:



the hydroxyl group being capable of migrating to the other nitrogen atom.

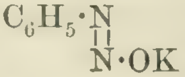
The latter formula provides an exceedingly probable constitution for the so-called *syn*-diazohydroxides and the corresponding metallic derivatives, for when one considers that the diazo-chloride yields the metallic derivative simply by admixture with caustic alkali at a very low temperature, in some cases below 0°, it seems reasonable to suppose that this change is accompanied by the smallest possible alteration in the constitution, such as is indicated above. When, however, the reaction is carried out at a high temperature, the quinonoid configuration is lost and the *iso*-salt is produced, thus:



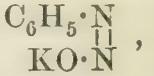
which is more in accord with the tautomeric nitrosoamine form than is the *anti*-configuration of Hantzsch.

From the above reasoning it is apparent that, as the constitution of the various diazo-compounds may readily be interpreted without the aid of the stereochemical theory, the terms *syn* and *anti* cannot be used. At the same time it is convenient to retain the name "diazonium" for what have up to this point been designated "diazo"-salts, and instead of "*syn*" and "*anti*" we have now "normal diazo-oxide" (for *syn*-diazotate) or simply "diazo-oxide" and "*iso*diazo-oxide" (for *anti*-diazotate), reverting to the older names.

The close chemical relationship between the diazo-oxides and the *iso*diazo-oxides are all readily explained by the formulæ here developed. The very slight capacity for coupling with phenols which is manifested by the *iso*-salt is explained by the fact that this is already an azo-compound, and the process may be regarded, not as a condensation, but as a displacement of the OK group by the C_6H_4·OK group. This difference in coupling power cannot, however, be explained by the stereochemical theory; indeed, one would almost expect the *anti*- to couple more readily than the *syn*-compound, for it is conceivable that if these really represented the configurations of the respective compounds



$$\begin{array}{r} C_6H_5\cdot N \\ \| \\ N\cdot OK \end{array}$$



$$\begin{array}{r} C_6H_5\cdot N \\ \| \\ KO\cdot N \end{array},$$

the *syn*-compound should couple more slowly than the *anti*-, owing to a greater possibility of steric hindrance.

CI.—*Experimental Investigation into the Process of Dyeing.*

By JULIUS HÜBNER.

NOTWITHSTANDING the great importance of a precise knowledge of the mechanism of the process of dyeing fibrous materials, this subject has not advanced considerably since the classic work of Walter Crum (Trans., 1863, **16**, 404). The main cause of this is perhaps that although many contributions to the question have been made, the experimental data upon which far-reaching conclusions have been based have in too many cases been altogether insufficient. The amount of really accurate quantitative data bearing on the manner in which colouring matters are absorbed by fibrous materials is quite insignificant when compared with the intricacy of the subject; many of the more comprehensive pieces of experimental work concerned are mentioned in the course of the present paper.

A considerable amount of evidence has been accumulated showing that the absorption of colouring matters by fibres is in many cases not due to the formation of definite chemical compounds nor to the formation of solid solutions of the ordinary kind. W. Crum compared the process of dyeing with the absorption of various materials by charcoal; von Georgievics (*Mitt. techn. Gewerbe-museums, Wien*, 1894) also showed that Magenta, &c., are absorbed by porous plate and by glass beads, and that the dyed products are not readily freed from the colouring matter by boiling water. The latter author further made a comparison of the mode in which colouring matters and tannic acid are taken up by cotton, wool, and asbestos in a fibrous and disintegrated or structureless condition; he found that in every instance the fibrous material absorbed larger quantities of dye than did the corresponding material in the structureless or powdered state. He also showed (*Monatsh.*, 1894, **15**, 705, and with Löwy, *ibid.*, 1895, **16**, 345) that the proportions in which such colouring matters as Indigo-carmine and Methylene-blue are absorbed by wool and cotton do not indicate the formation of solid solutions. Schmidt (*Zeitsch. physikal. Chem.*, 1894, **15**, 56) has ascertained that iodine is not absorbed by charcoal from benzene or alcoholic solution in accordance with Henry's law, and the general results of these investigations have been confirmed by Walker and Appleyard (Trans., 1896, **69**, 1334), who examined the equilibrium established between silk and picric acid both in aqueous and alcoholic solutions.

The recent work of H. Freundlich (*Habilitationsschrift*, Leipzig, 1906), who measured accurately the absorption of a number of substances by purified charcoal from solution in different solvents, establishes with even greater precision the conclusion to be derived from the previous work.

The chemical theory of the dyeing process has been largely supported by experimental work having for its object the drawing of close analogies between dyeing and actual typical chemical reactions; in view of the obvious weaknesses of the analogies thus derived and the striking nature of the parallels between the processes of dyeing and of physical or mechanical absorption briefly indicated above, it seemed very desirable that this aspect of the subject should be further examined. This further examination should not include simply the determination of the proportions in which colouring matters, &c., are absorbed by various materials, as has been previously done, but should also have for its object a careful comparison of the behaviour of the different types of materials during and after the dyeing operation.

As a preliminary to this extension of the scope of the analogy to be drawn between dyeing and physical or mechanical absorption further exact information was obtained as to the mode in which the absorption of colouring matters by fibrous materials is influenced by the degree of disintegration of the latter; the fibrous nature of the material used was not entirely destroyed in these experiments, but different series of observations were made with material of different mean length of fibre.

It is well known that fibres such as cotton, which have been converted into paper pulp by mechanical treatment in the presence of water, behave differently towards colouring matters than do the fibres in the original state.

A quantity of material was prepared by boiling cotton yarn from American cotton twice under pressure in the usual manner with caustic soda; it was then well washed, and dried in the stove for several days. The cotton was not bleached in order to avoid the possible formation of oxycellulose. The dried material then contained 5·6 per cent. of moisture; part of it was cut into pieces of about 2 inches in length, whilst the remainder was subjected to mechanical disintegration for various periods in the beating engine. The various portions required for use in the absorption experiments were withdrawn from the beater at the expiration of 1·5, 3, 4·5 and 6 hours' treatment respectively. The average length of fibre left in the beaten material at the end of the several periods mentioned was measured in the usual way, and the results are stated in Table I; the speed at which disintegration proceeds obviously diminishes as the time of beating increases.

For each of the absorption experiments the weight of cotton or pulp used corresponded to 20 grams of absolutely dry fibres. The absorption tests were carried out with the basic colour Night-blue, because the amount present in the dye-bath can be readily and accurately ascertained by titration with a solution of Naphthol-yellow S (Rawson, *J. Soc. Dyers and Colourists*, 1888, **4**, 82). In each case 20 grams of the material were immersed in a solution of 0·2 gram of Night-blue in 900 c.c. of water; the experiments were conducted at the ordinary temperature in Jena glass flasks, which were frequently shaken in order to prevent uneven absorption. It was found that equilibrium between dye solution and fibres was established in about 48 hours. Table I shows the actual weight of dye absorbed by the 20 grams of dry material in the various stages of disintegration and after different periods of immersion; it also states (in brackets) the proportion of the dye used which is absorbed by the material.

TABLE I.

		Gram dye absorbed.				
	Time of immersion in hours.	Original fibres.	1·5 hours' beating.	3 hours' beating.	4·5 hours' beating.	6 hours' beating.
Average length of fibre in mm. ...		23·0	2·5	1·5	1·1	0·7
Cotton............	1	0·0289	0·1044	0·1137	0·1168	0·1245
		(0·1445)	(0·522)	(0·5685)	(0·584)	(0·6225)
	6	0·049	0·1177	0·1183	0·1184	0·1245
		(0·245)	(0·5885)	(0·5915)	(0·592)	(0·6225)
	18	0·0551	0·1183	0·1183	0·122	0·1245
		(0·2755)	(0·5915)	(0·5915)	(0·61)	(0·6225)
	72	0·644	0·1214	0·1269	0·1294	0·1306
		(0·322)	(0·607)	(0·6345)	(0·647)	(0·653)
Average length of fibre in mm. ...		29·0	3·12	2·2	0·7	0·4
Wool	1	0·0305	0·0351	0·0382	0·0459	0·049
		(0·1525)	(0·1755)	(0·191)	(0·2295)	(0·245)
	6	0·0366	0·0382	0·0413	0·0462	0·0521
		(0·183)	(0·191)	(0·2065)	(0·231)	(0·2605)
	18	0·0413	0·0428	0·0443	0·047	0·0521
		(0·2065)	(0·214)	(0·2215)	(0·235)	(0·2605)
	72	0·0521	0·0521	0·0521	0·0521	0·0521
		(0·2605)	(0·2605)	(0·2605)	(0·2605)	(0·2605)
Percentage of water retained at 60°		3·24	2·13	2·33	1·47	1·51

It is noteworthy that the unbeaten cotton yarn shows a constantly increasing absorption during the 72 hours of immersion, whilst the most highly disintegrated material absorbs colouring matter very rapidly during the first hour of immersion, and but a very small further amount of dye is taken up during the remaining 71 hours of immersion. It must thus be concluded that in the case of cotton the degree of subdivision of the fibre greatly influences both the total proportion of dye absorbed and the rate at which absorption occurs. It is remarkable that the most highly disintegrated material was found coloured to about the same depth of shade as the original yarn, although it had absorbed more than twice the proportion of colouring matter. This observation is in accordance with practical experience in the dyeing of basic dyes on paper pulp.

The fact that the wool fibre differs very materially from the cotton fibre as regards its structure and its dyeing properties made it of interest to study this fibre under similar conditions. A quantity of unbleached woollen rags (flannel) was scoured with ammonia, so as to remove any fatty matter, washed free from ammonia, torn to pieces of approximately equal size, and then disintegrated in the beating engine. Whilst no difficulty was experienced in weighing the cotton pulp, in the case of the wool the water separated so quickly from the wool pulp as to render this impracticable; the different grades of pulp were therefore removed from the beating engine, freed as far as possible from water by pressing, and then left for about four days in a large drying stove at a temperature of 60°. After this treatment the retained moisture was in each case determined; the results are stated in Table I, as are also the average lengths of the fibre. In each experiment 10 grams of absolutely dry fibre were immersed at the ordinary temperature in 900 c.c. of liquor containing 0·2 gram of Night-blue. Previous thereto, and for the purpose of evenly wetting out the dry fibres, 200 c.c. of boiling water were added to each batch of fibre and allowed to stand for 24 hours before adding the dye solution; the fibres in the finest state of disintegration were found to felt together during the drying, and for the purpose of preventing uneven penetration and absorption of the dye boiling water was added as described, and the whole shaken for two hours on a mechanical shaking apparatus.

The amount of colouring matter absorbed by 10 grams of wool, in the various degrees of disintegration and after different periods of immersion, is stated also in Table I. The results obtained with disintegrated wool fibres differ very materially from those obtained with cotton. Equilibrium between the dye in solution and the fibres is, as before, established in less than 72 hours; the amount of dye absorbed after 72 hours' immersion is, however, the same, whether the fibres are in the original state or in a very finely disintegrated condition. The original fibres absorb the colouring matter gradually, maximum absorption being obtained after between 18 and 72 hours of immersion; the finely disintegrated fibres (six hours' beating) behave quite differently in that maximum absorption is obtained after between one and six hours of immersion. The depth of shade of the dyed fibres after 72 hours' immersion is uniform throughout and independent of the degree of disintegration; this contrasts with the results obtained with cotton.

From this set of experiments it must be concluded that the degree of disintegration of the wool fibre influences the speed with which equilibrium is established as between fibre and dye, but does not influence the proportion of colouring matter ultimately absorbed. It might be suggested that the beating of the cotton or wool in contact with water produces some chemical change in the material; it was therefore desirable also to examine some fibrous material of simpler physical character than either cotton or wool, more especially with the view of ascertaining more directly whether the amount of fibrous surface exposed to the action of the dye-bath influences the proportion of dye absorbed. For this purpose artificial silk of two kinds, differing only in that they consisted of fibres of the average diameters 0·0299 mm. and 0·184 mm. respectively was used. Quantities of these two silks were cut into lengths of about 2 inches, and 10 grams of each (dry weight) were immersed for 72 hours in 750 c.c. of solution containing 0·15 gram of Night-blue. The fine silk absorbed 0·0986 gram, and the coarse silk 0·0558 gram of colouring matter. It is thus clear that the finer silk, which exposes the larger surface, absorbs considerably more dye than the coarser material, and a direct indication is obtained that in the absorption of Night-blue by artificial silk the proportion taken up is roughly proportional to the surface exposed by the fibrous material.

Further confirmation of this result was obtained by studying the absorption of Night-blue by a chemically inert substance, namely, emery powder; two samples of levigated emery, the one very fine and the other much coarser, were used. One hundred grams of each kind were immersed for periods of 1, 6, 18, and 72 hours in 750 c.c. of water containing 0·15 gram of Night-blue. The results were as follows:—

TABLE II.

	Gram dye absorbed.			
Time of immersion in hours	1.	6.	18.	72.
Coarse emery..................	0·0081	0·0167	0·0263	0·05
	(0·0587)	(0·1113)	(0·175)	(0·333)
Fine emery.....................	0·05	0·0618	0·09	0·09
	(0·3333)	(0·412)	(0·6)	(0·6)

The behaviour of the fine and coarse emery is clearly very similar in kind to that of the fine and coarse artificial silks, and also to that of the various grades of disintegrated cotton fibre. It is therefore concluded that the amount of surface exposed to the action of the dye solution greatly influences the proportion of dye absorbed, not only in the case of a material such as emery, which is certainly chemically inert, but also in that of cotton or artificial silk.

In the above series of experiments a distinct analogy is traceable between the action of cotton and artificial silk and of emery powder on dye solutions.

It seemed desirable further to extend the investigation for the purpose of ascertaining whether or not the indicated analogy has a real physical significance or not. Cotton, wool, silk, &c., were therefore dyed with a number of colouring matters typical of the different classes of coal-tar dyes, for the purpose of comparison with parallel trials carried out with such chemically inert substances as graphite, blood charcoal, China clay, &c.

As the quantity of colouring matter absorbed by materials varies widely with the conditions of dyeing, identical methods were adopted in every case; no attempt was made to obtain absolute results concerning the absorption of colouring matter, as for the present purpose the primary object of the work was the obtaining of values which are rigidly comparable among themselves, but in each case the time of immersion, the temperature, the mode of shaking, &c., were identical.

The colouring matter remaining in the dye bath was determined by titration in the cases of Night-blue and Naphthol-yellow S, and by the Dubosq colorimeter in all other cases.

Table III gives the results obtained by immersing the materials named in the first column (10 grams dry weight) in 750 c.c. of water containing 0·25 gram (in the case of charcoal 3·5 grams) of Night-blue; column 2 shows how much colour is absorbed during 72 hours' immersion in the cold; column 3 gives the amount absorbed during 72 hours' immersion in the cold followed by one hour's heating to 95°, the liquor being drawn off at this temperature; column 4 gives results obtained in the same way as those of column 3, with the difference that the solution after heating for an hour at 95° was allowed to cool and to remain in contact with the material for another period of 72 hours before examination. The numbers enclosed in brackets in this and the other tables state the proportions of colouring matter corresponding to the actual weights absorbed.

The graphite used was in the state of very fine powder, and the blood charcoal was the specially purified material supplied by Merck (Darmstadt).

TABLE III.

	Gram dye absorbed.		
	Cold.	Hot.	Cooled.
Cotton	0·036	0·04	0·04
	(0·144)	(0·16)	(0·16)
China clay	0·1693	0·17	0·172
	(0·6772)	(0·68)	(0·688)
Graphite	0·2449	0·2474	0·249
	(0·9796)	(0·9896)	(0·996)
Wool	0·05	0·23	0·2486
	(0·2)	(0·92)	(0·994)
Silk	0·236	0·246	0·249
	(0·944)	(0·984)	(0·996)
Charcoal	3·123	3·495	3·5
	(0·8923)	(0·9987)	(1·0)

Parallel experiments were also made with lamp-black, the filtration of the solutions presented great difficulties and the absorption values were therefore only approximately ascertained. It was, however, found that the lamp-black absorbs basic dyes freely, more when heated than in the cold, and a further quantity of dye is absorbed when the liquor is allowed to cool after heating. It thus behaves similarly to charcoal.

It is concluded from the results given in Table III that the absorption of the basic colouring matter Night-blue proceeds in a similar manner in every instance independently of whether animal or vegetable fibres or inorganic absorbents are used.

After dyeing, all the materials were separated from the bath and washed with distilled water until the wash-water became colourless; this, even with graphite, China clay, and charcoal, resulted after a few washings, the dye thus being retained by the material in such a manner that it does not "bleed" into water. It is generally supposed that after charcoal has absorbed colouring matters from solution, the dye is very loosely held by the absorbent and can be completely removed, although slowly, by repeated washing in distilled water; this assertion has been used to support the contention that a number of dyeing phenomena cannot arise from mere absorption (Freundlich, *loc. cit.*, 91).

Since it is now definitely established that charcoal, graphite, &c., absorb Night-blue just as do textile fibres, the colouring matter not being washed out by subsequent treatment with water, the objection referred to must be regarded as groundless.

The analogy between the absorption of colouring matters by fibrous materials and charcoal, &c., can be further extended by examining the behaviour of the dyed materials towards a neutral soap solution; the dyed cotton, wool, silk, graphite, China clay, and charcoal bleed freely in hot Marseille soap solution.

The very complete analogy of behaviour existing between the dyeing of fibrous materials and inorganic or inert absorbents when the basic dye Night-blue is used having been thus demonstrated, it became desirable to extend the work to the study of the absorption of acid colouring matters towards the same materials. As typical representatives of the three groups of acid colouring matters were selected the nitro-compound Naphthol-yellow S, the azo-colouring matter Ponceau RR, and the sulphonated basic dye Acid-magenta.

TABLE IV.

	Dye used, grams.	Gram dye absorbed.					
		Without acid.			With 4 per cent. H_2SO_4.		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·08	0·0	0·0	0·0	0·005	0·005	0·005
	—	—	—	—	(0·0625)	(0·0625)	(0·0625)
China clay	0·08	0·0	0·0	0·0	0·0024	0·0035	0·0024
	—	—	—	—	(0·03)	(0·0438)	(0·03)
Graphite	0·08	0·018	0·0067	0·018	0·017	0·013	0·018
	—	(0·0225)	(0·0084)	(0·0225)	(0·2125)	(0·1625)	(0·225)
Wool	0·6	0·063	0·013	0·063	0·5956	0·566	0·5956
	—	(0·105)	(0·0217)	(0·105)	(0·9927)	(0·9433)	(0·9927)
Charcoal	5·5	4·35	3·0	4·35	5·437	5·363	5·402
	—	(0·7909)	(0·5455)	(0·7909)	(0·9886)	(0·9751)	(0·9822)

In this table the amounts of Naphthol-yellow S absorbed by 10 grams of (dry) material, dyed both with and without the addition of sulphuric acid to the dye bath, are given; the conditions, without acid, are therefore the same as in the Night-blue experiments.

It is to be noticed that, without acid, cotton and China clay do not absorb Naphthol-yellow S, and that graphite also absorbs little and much less in the hot than in the cold. Wool and charcoal both absorb very strongly, and in each case much less is absorbed in the hot than in the cold. After dyeing the materials were washed with water; the small quantity of colouring matter absorbed by the graphite is very readily and completely removed by a few washings with distilled water. The behaviour of the other dyed materials is conveniently discussed together with the results obtained by the addition of 4 per cent. of sulphuric acid to the dye bath, also contained in Table IV.

Naphthol-yellow S becomes considerably lighter in shade when sulphuric acid is added to its solution. To counteract this in titrating with Night-blue phenolphthalein was added to the solution, which was then made slightly alkaline by *N*/10-caustic soda. A drop of acetic acid was afterwards added so as slightly to acidify the solution.

The quantities of colouring matter absorbed are very small in the case of cotton, graphite, and China clay, as compared with those absorbed by wool; further, the dye is in the former instances completely removed by a few washings with water. Dyeing of the cotton, graphite, &c., in the proper sense of the word, therefore does not take place. The following results were obtained by the comparative washing with water of wool and charcoal, dyed with and without the addition of acid to the dye bath. In both cases the wash-water apparently became colourless much sooner when acid was used in the dye bath, the dyeings without acid running more freely and the wash-water remaining slightly coloured even after prolonged washing.

With a view to determine whether very slow washing would remove still further quantities of colouring matter, the samples of charcoal dyed with and without the addition of acid were washed by the aid of the pump. When no acid had been used, about three weeks' washing was required for the removal of practically all the colouring matter absorbed by the charcoal. The amount was checked by collecting all the wash-water and titrating it with Night-blue. A much larger amount of water was required to exhaust the colouring matter from charcoal dyed with the addition of acid; but after about eight weeks' washing titration of the wash-water showed that all the dye absorbed had been removed.

The dyed samples of wool were washed for a considerable time by repeated soakings and running off the wash-water, with similar results to those obtained with the corresponding samples of charcoal.

It is important to note that the running of the colouring matter seems to proceed fairly rapidly up to a certain point, after which much water and considerable time are needed for the removal of the remaining portion. Fowler and Gaunt have drawn attention to a very similar fact, namely, that the washing out of ammonium chloride absorbed by gravels proceeds very rapidly until a certain point is reached, but very slowly after this.

Table V. refers to dyeing with Ponceau RR, with and without the addition of acid to the dye bath.

TABLE V.

		Gram Ponceau RR absorbed.					
		Without acid.			With 4 per cent. H_2SO_4.		
	Dye used, grams.	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·2	0·0	0·0	0·0	0·0	0·0	0·0
Graphite	0·2	0·0462	0·0	0·0463	0·0	0·0	0·0
	—	(0·231)	(0·0)	(0·2315)	—	—	—
Wool	1·0	0·0889	0·064	0·12	0·387	0·807	1·0
	—	(0·0889)	(0·064)	(0·12)	(0·387)	(0·807)	(1·0)
Silk	1·0	0·19	0·096	0·192	0·264	0·576	0·713
	—	(0·19)	(0·096)	(0·192)	(0·264)	(0·576)	(0·713)
Charcoal	5·5	5·31	5·438	5·5	5·428	5·473	5·5
	—	(0·9655)	(0·9887)	(1·0)	(0·9869)	(0·9951)	(1·0)

(*a*) Without the addition of acid:—Cotton absorbs no Ponceau either in the cold or hot. Graphite absorbs a small amount in the cold, which, however, is expelled on heating and is re-absorbed on cooling. Washing removes the colouring matter absorbed by the graphite quickly and completely. Wool and silk absorb less colouring matter in the hot than in the cold, whilst charcoal absorbs more in the hot. In every instance the maximum amount of colouring matter is absorbed after cooling.

(*b*) With the addition of acid:—Cotton and graphite do not absorb colouring matter, either hot or cold. Wool, silk, and charcoal behave analogously in that they absorb more dye in the hot than in the cold, and take up a further quantity on cooling. On washing with water it is distinctly noticeable that the materials dyed with the addition of acid are more quickly freed from the loosely-held colouring matter than those dyed without the acid. More colouring matter is extracted from the charcoal than from either wool or silk, probably because the charcoal has been completely saturated with colouring matter and takes up more than five times as much as the wool; this excess, which is doubtless held superficially, is washed away more readily, whilst the main bulk of the colouring matter is held much more firmly. Wool and charcoal dyed without the addition of acid both lose a little colouring matter with cold water, more with hot water, and still more when soda and soap are applied. The materials dyed with the addition of acid behave similarly on the whole, but no colouring matter is extracted from the wool by cold water.

It was deemed of interest to ascertain whether charcoal containing the same proportion of colouring matter as the wool would hold it in a similar manner. For this purpose 10 grams of (dry) charcoal were allowed to absorb 1 gram of Ponceau RR, with and without the addition of acid, respectively. Charcoal treated in this manner does not allow any of the colouring matter to bleed, either into cold or hot water, and none can be extracted if soda is added to the wash-water; the colouring matter is therefore more firmly held by the charcoal than by the wool. On boiling with neutral soap solution the colouring matter, however, "bleeds" freely. Silk dyed with Ponceau, both with and without the addition of acid, behaves similarly to wool and charcoal, but "runs" more freely than either.

TABLE VI.

		Gram Acid-magenta absorbed.					
	Dye used, grams.	Without acid.			With 4 per cent. H_2SO_4.		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·1	0·0	0·0	0·0	0·0	0·0	0·0
Graphite	0·1	0·0	0·0	0·0	0·0	0·0	0·0
Wool	0·5	0·0334	0·0212	0·0518	0·386	0·467	0·5
	—	(0·0668)	(0·0424)	(0·1036)	(0·772)	(0·934)	(1·0)
Silk	0·5	0·222	0·067	0·233	0·469	0·371	0·477
	—	(0·444)	(0·134)	(0·466)	(0 938)	(0·742)	(0·954)
Charcoal	3·25	2·905	2·5	2·784	3·2387	2·803	3·2394
	—	(0·8938)	(0·7692)	(0·8566)	(0·9965)	(0·8625)	(0 9967)
Lamp black......	1 0	0 317	0·058	0·244	0·5296	0·1874	0·3649
	—	(0·317)	(0·058)	(0·244)	(0·5296)	(0·1874)	(0·3649)

Experiments carried out with Acid-magenta show that no colouring matter is absorbed by cotton or graphite if dyed either with or without the addition of acid to the dye-bath. Wool, silk, and charcoal, dyed without the addition of acid, absorb less colouring matter in the hot than in the cold, but take up more on cooling. Silk and charcoal, dyed with the addition of acid, exhibit parallel behaviour in that they absorb less colouring matter in the hot than in the cold, but take up slightly more on cooling. Wool, under these conditions, absorbs more dye hot than cold, and still more on cooling.

On washing the Acid-magenta dyeings it was in every instance noticed that more colouring matter is removed than in the case of Ponceau RR, the dyeings with the addition of acid being invariably faster than those without acid. The colouring matter is more readily washed out from the silk than from charcoal or wool.

Experiments similar to those carried out with Ponceau (1 gram of colour) were made with charcoal (10 grams), with and without the addition of acid. The colouring matter is much more strongly held by the charcoal when acid has been added to the dye-bath. Soap and soda have a similar action on wool, silk, and charcoal in removing the dye.

It is thus shown that the analogy pointed out between the absorption of basic dyes by fibrous and inert absorbents extends with remarkable precision to the absorption of acid colouring matters; but in the latter case a differentiation is to be observed. Graphite and China clay absorb the acid colouring matters in exactly the same kind of way as do fibres of vegetable origin, like cotton, whilst charcoal and the fibres of animal origin, such as wool and silk, behave similarly; the two classes of behaviour thus distinguished are strikingly different.

It was still necessary to ascertain whether the analogy also extends to the behaviour of the absorbents towards the colouring matters which dye cotton direct; as one of these Diamine Sky-blue **FF** was selected, because, whilst being a typical dye of this class, it behaves quite specially towards wool. In a dye-bath containing a small amount of sodium carbonate this colouring matter, whilst dyeing on cotton, does not dye wool. In the first series of experiments no addition was made to the dye-bath, whilst in the second series 15 grams of sodium sulphate, and in the third 0·6 gram of sodium carbonate, was added to the dye-bath.

From Table VII it will be seen that cotton, artificial silk, and graphite absorb less colouring matter in the hot than in the cold, whilst silk, China clay, and charcoal absorb more in the hot than in the cold. Wool absorbs only a trace of colouring matter after heating and cooling; the amount absorbed is, however, too small to be measured accurately.

From the second series of experiments (dyeing with the addition of sodium sulphate) it will be noticed that cotton is the only material which absorbs less colouring matter in the hot than in the cold. Wool, silk, artificial silk, and charcoal take up more in the hot than in the cold, and a further quantity on cooling. Graphite and China clay, although behaving like the latter, yet on cooling absorb less dye than in the hot.

The third series (addition of sodium carbonate to the dye-bath) shows that wool and silk absorb no colouring matter. Cotton and artificial silk take up less in the hot than in the cold, but on cooling after heating a further quantity is absorbed. Graphite takes up practically the same proportion of colouring matter under the several conditions. China clay takes up more in the hot but gives it up on cooling. Charcoal behaves as in the former two instances.

The following classification of the results facilitates their comparision:—

(*a*) Material dyed without any addition to the dye-bath:—Cotton and graphite both "bleed" distinctly with cold water, cotton rather more freely than graphite. Both "bleed" more freely in hot water and still more colouring matter is removed when sodium carbonate or soap is added to the water. Silk "bleeds" hardly appreciably in the hot, a little more when sodium carbonate is added, and still more with soap.

(*b*) Material dyed with the addition of sodium sulphate:—Cotton "bleeds" less than in (*a*), either hot or cold; soda and soap remove the dye more freely. Graphite does not "bleed" appreciably, either hot or cold, and very little with sodium carbonate or soap. It is quite evident that the graphite holds the dye more strongly than does the cotton. The silk "bleeds" comparatively less than in (*a*), especially when it is considered that a much greater proportion of colouring matter has been absorbed.

TABLE VII.

Material, 10 grams (charcoal, 5 grams). Dye-bath (750 c.c.) containing 0·4 gram (in the case of charcoal, 3·0 grams) of dye.

	Gram Diamine Sky-blue FF. absorbed.								
	No addition.			With 15 grams Na_2SO_4.			With 0·6 gram Na_2CO_3.		
	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·0442	0·0075	0·0578	0·3171	0·2269	0·3654	0·0712	0·0471	0·121
	(0·1105)	(0·0188)	(0·1445)	(0·7927)	(0·5672)	(0·9135)	(0·178)	(0·1178)	(0·3025)
Artificial silk	0·0308	0·016	0·08	0·3059	0·32	0·4	0·0572	0·0308	0·1091
	(0·077)	(0·04)	(0·2)	(0·7647)	(0·8)	(1·0)	(0·143)	(0·077)	(0·2728)
Graphite	0·3714	0·1757	0·3035	0·1932	0·2378	0·1333	0·0757	0·08	0·0757
	(0·9285)	(0·4393)	(0·7587)	(0·483)	(0·5945)	(0·3333)	(0·1892)	(0·2)	(0·1893)
China clay	0·0571	0·0735	0·0429	0·0471	0·1	0·0364	0·0308	0·1126	0·016
	(0·1428)	(0·1837)	(0·1073)	(0·1178)	(0·25)	(0·091)	(0·077)	(0·2815)	(0·04)
Wool........................	0·0	0·0	trace	0·0096	0·1042	0·188	0·0	0·0	0·0
	—	—	—	(0·024)	(0·2605)	(0·47)	—	—	—
Silk	0·2323	0·3117	0·3826	0·3529	0·3633	0·4	0·0	0·0	0·0
	(0·5807)	(0·7792)	(0·9565)	(0·8823)	(0·9083)	(1·0)	—	—	—
Charcoal	1·743	2·9659	3·0	1·816	2·8286	2·9386	1·7	2·95	3·0
	(0·581)	(0·9886)	(1·0)	(0·6053)	(0·9429)	(0·9795)	(0·5666)	(0·9833)	(1·0)
	Gram Congo-rubine absorbed.								
Cotton	0·1273	0·0889	0·1447	0·2942	0·2208	0·3045	0·1778	0·1436	0·1895
	(0·3183)	(0·2222)	(0·3617)	(0·7355)	(0·552)	(0·7612)	(0·4445)	(0·359)	(0·4737)
Graphite	0·3527	0·2889	0·3487	0·3385	0·2095	0·3375	0·1561	0·1576	0·156
	(0·8817)	(0·7222)	(0·8718)	(0·8462)	(0·5238)	(0·8438)	(0·3903)	(0·394)	(0·39)
Wool........................	0·1059	0·1531	0·1949	0·2333	0·2676	0·3692	0·1059	0·1241	0·15
	(0·2647)	(0·3827)	(0·4872)	(0·5833)	(0·669)	(0·923)	(0·2648)	(0·3104)	(0·375)
Charcoal	2·1304	2·975	3·0	2·3846	2·9385	2·961	2·3939	2·92	3·0
	0·7101)	(0·9917)	(1·0)	(0·7949)	(0·9795)	(0·987)	(0·798)	0·9733)	1·0)

Artificial silk, if compared with cotton, "bleeds" distinctly less, either with or without the addition of sodium sulphate. The dyed wool scarcely "bleeds" in hot water, but the addition of soap or sodium carbonate removes the colouring matter very freely. Charcoal, dyed both with or without the addition of sodium sulphate, resists the action of hot or cold water very well. Sodium carbonate does not remove the dye to any appreciable extent, but with soap and sodium carbonate the colour "runs" very freely. It therefore behaves very similarly to wool.

With the exception of a few dyes, such as the Diamine Sky-blue FF, used above, the colouring matters dyeing cotton direct show a great affinity for the wool fibre; it was therefore of importance to study a dye of this class which dyes wool readily, and for this purpose Congo-rubine was selected. The results obtained are also given in Table VII.

It is seen that when dyed with Congo-rubine, without any other addition to the dye-bath, cotton behaves similarly to graphite, whilst wool is dyed like charcoal. When dyed with the addition of sodium sulphate, cotton, as before, behaves analogously to graphite, and wool to charcoal. With the addition of sodium carbonate wool behaves like charcoal, whilst the cotton absorbs slightly less in the hot than in the cold; the absorption of the colouring matter by graphite is practically uninfluenced by the temperature changes. Both the dyed cotton and graphite "bleed" very little with cold water, more distinctly with hot water, and still more freely with the addition of sodium carbonate or soap. The dyed wool and charcoal also behave very similar in that they "bleed" but little with hot water and more freely with sodium carbonate or soap. The dyed charcoal and wool both bleed comparatively less when dyed with the addition of sodium sulphate.

It is well known that both the acid colouring matters and those which dye cotton direct are capable of forming lakes with the basic dyes. C. O. Weber (*J. Soc. Chem. Ind.*, 1894, **13**, 121) states that wool dyed with Scarlet R absorbs Magenta to the same extent as does white wool, and that this is not due to a simple lake formation between the two colouring matters, but to the formation of a compound lake between the two colouring matters and the wool fibre. To prove this he points out that lakes formed between these dyes in the absence of wool are soluble in alcohol, whilst "in treating with alcohol the hank dyed with Scarlet and Magenta, only a very small quantity of Magenta, but not the faintest trace of Scarlet is dissolved."

Having found, as pointed out above, that colouring matters are, in many instances, absorbed similarly by fibres and by substances such as charcoal, graphite, &c., it seemed of interest to repeat these experiments both with fibres and inorganic absorbents. For this purpose wool was dyed with Scarlet RR, well washed and "topped" with Night-blue, and afterwards throughly rinsed. Charcoal was treated in a similar manner. On treating the dyed wool repeatedly with alcohol practically all the Night-blue was extracted, whilst the Scarlet remained unaltered on the wool. Absolute alcohol acts neither so quickly nor so completely as alcohol to which a very small quantity of water has been added. The compound colouring matter resists treatment with cold water very well, but, on heating, the Scarlet dissolves out slowly whilst the blue remains on the fibre.

By repeated washing (soaking) of the wool in hot water practically all the Scarlet may be removed, whilst the Night-blue is hardly affected. On adding a little ammonia to the water used for dissolving out the Scarlet and by boiling for about 30 minutes the Scarlet was removed completely, whilst the Night-blue remained on the fibre. A small quantity of alcohol added to the water used for the washing also accelerates the solution of the Scarlet and by applying water and alcohol in about equal quantities both colouring matters may be removed slowly from the fibres. Each of these experiments was repeated with the substitution of charcoal for the wool; in every case the charcoal dyeings behaved exactly like the wool dyeings.

The behaviour of colouring matters dyeing cotton direct when "topped" with basic dyes was next studied; for this purpose cotton cloth was dyed with Benzopurpurin 4B, thoroughly washed and "topped" with Night-blue, and finally well washed. Graphite and charcoal were treated in a similar manner.

It was observed that the basic dye could be readily extracted with alcohol, and more rapidly still with alcohol to which a small quantity of water had been added, so that finally the red was left practically pure on the cloth. Benzopurpurin is slightly soluble in alcohol, and the shade stripped off the blue is therefore a trace lighter than the original one. On boiling the dyed samples with water the red dissolves out very slowly. To accelerate this operation, white mercerised cloth, which, as is well known, attracts very strongly colouring matters dyeing cotton direct, was boiled with the dyed cloth. By adopting this course the Benzopurpurin was nearly completely removed after prolonged boiling, frequent changes of water and of white mercerised cloth being made. Benzopurpurin can be removed with the aid of mercerised cotton, as just described, but much more rapidly and more completely by boiling water containing a trace of sodium carbonate. During this treatment the shade of the Night-blue is reddened by the action of the sodium carbonate; after extraction of the red, however, steeping of the cloth in water slightly acidified with acetic acid completely restores the colour. On substituting dyed charcoal and graphite for the dyed cotton in the above set of experiments it was found that they exhibit behaviour closely analogous to that of the cotton.

The colour lakes produced from basic and acid colouring matters or of basic dyes and colouring matters dyeing cotton direct are thus very fast to cold water when dyed on textile fibres and on the inert absorbents mentioned, and the acid or the direct dyeing colouring matter respectively is only slowly removed from either type of absorbents by hot water.

It is impossible to avoid the conclusion from these results that the dyeing operation in these instances also is of a purely mechanical character.

In the foregoing experiments the textile fibres used have been replaced by inert materials, such as charcoal, graphite, &c., and it seemed desirable to make a series of experiments on the absorption of substances other than coal-tar dyes by these materials. The following experiments were undertaken with a view to ascertain whether iodine and colouring matters are absorbed in a similar manner by wool. Ten grams of (dry) wool were immersed in 750 c.c. of potassium iodide solution containing 1·905 grams of free iodine. The time of immersion varied as shown in Table VIII.

TABLE VIII.

Time of immersion in hours	1.	6.	18.	72.
Gram absorbed ……………	1·32	1·62	1·767	1·848
	(0·6929)	(0·8504)	(0·9276)	(0·9701)

Inspection of the table shows that the absorption of iodine by wool proceeds similarly to the absorption of Night-blue.

A comparison was next made of the mode in which iodine was absorbed by textile fibres and by inert absorbents. Table IX.

TABLE IX.

10 grams (dry) of material immersed 72 hours in 750 c.c. of potassium iodide solution containing 7·62 grams of free iodine.

	Grams absorbed.			Grams absorbed.	
Cotton…… …	0·136	(0·0178)	Wool ………	4·4	(0·5774)
Graphite ……	0·9	(0·1181)	Charcoal ……	7·35	(0·9646)
China clay …	0·56	(0·0735)			

The table shows that cotton and China clay absorb a small amount of iodine, whilst graphite absorbs rather more; wool and charcoal absorb very large quantities. Washing with water alone, removes the iodine very quickly and completely from cotton, China clay and graphite. Wool and charcoal retain the iodine much more firmly, a large amount of iodine remaining on both materials after washing with water. The colour of the wool containing iodine is a deep brown orange, and the iodine can be removed completely from both wool and charcoal by solvents such as alcohol or potassium iodide.

These results, therefore, still further extend the analogy of the absorption of a substance from solution in water by fibrous materials, such as cotton and wool, and by inert absorbents, such as graphite, China clay, and charcoal. It is also remarkable that iodine behaves towards all these absorbents similarly to acid dyes.

The foregoing absorption experiments prove conclusively that dyeing with basic colouring matters, with the three different types of acid dyes and with the colouring matters dyeing cotton direct, proceeds in a closely analogous manner independently of whether textile fibres or inert substances, such as charcoal, graphite, &c., are employed as absorbents. It may therefore be safely concluded that all these dyeing processes are due to purely physical or mechanical absorption. The correctness of this view is strongly supported by the results obtained on comparing the action of hot and cold water, of sodium carbonate, soap, &c., on the dyed materials, both fibres and inorganic absorbents exhibiting a remarkable degree of analogy of behaviour towards these treatments.

A number of results have also been obtained with other absorbents, such as finely-divided silver and copper, Kieselguhr, &c.; these substantiate the close analogies pointed out above, and their detailed description is therefore unnecessary in the present connexion.

The investigation is being extended so as to embrace the processes involved in other well known dyeing operations.

The author desires to express his thanks to his colleague, Prof. W. J. Pope, F.R.S., for the interest which he has taken in this investigation. He also desires to acknowledge the valuable services rendered by his assistant, Mr. Sidney H. Higgins, M.Sc., in connexion with the large amount of experimental work involved.

Municipal School of Technology,
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CII.—*Brazilin and Hæmatoxylin. Part VII.* Synthesis of Derivatives of Hydrindene closely allied to Brazilin and Hæmatoxylin.*

By William Henry Perkin, jun., and Robert Robinson.

During the course of a long series of researches on brazilin, it has been shown that this substance is readily converted into trimethylbrazilin when it is treated with caustic potash and methyl iodide or sulphate. The action of oxidising agents on trimethylbrazilin was then carefully investigated and the results obtained proved conclusively that the constitution of trimethylbrazilin must be represented by

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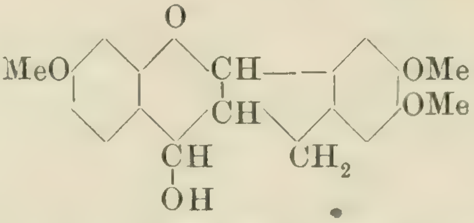
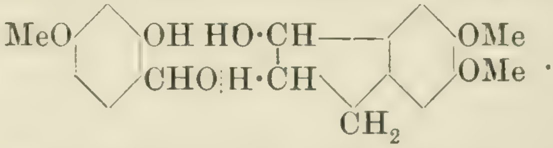
* Part I (Trans., 1901, **79**, 1396), Parts II and III (Trans., 1902, **81**, 221, 235), Parts IV, V, and VI (Trans., 1902, **81**, 1008, 1040, 1057). Proc., 1906, **22**, 160 refers to this paper; *ibid.*, 132, should be Part VIII.



or by some formula very closely allied to this. With the object of further testing the validity of this expression we have, during the last two years, been engaged in a series of synthetical experiments on the preparation and properties of a large number of substances closely allied to trimethylbrazilin, and in the present communication we give an account of the results obtained during the course of one group of these investigations. When the experiments on brazilein and hæmatein, on which we are at present engaged, are completed we hope to have the opportunity of discussing in detail the bearing of all the results obtained on the question of the constitutions of brazilin and hæmatoxylin.

If, in the formula of trimethylbrazilin given above, the hydroxychroman ring is opened by the addition of the elements of water, we obtain, for the product of hydrolysis, the following expression :



If then the further assumption is made that the molecule suffers disruption at the point indicated by the dotted line, the products of scission are clearly *p*-methoxysalicylaldehyde and 1-hydroxy-5 : 6-dimethoxyhydrindene.* Since trimethylbrazilin is so closely allied to hydrindene,

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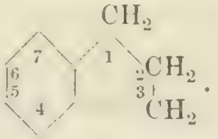
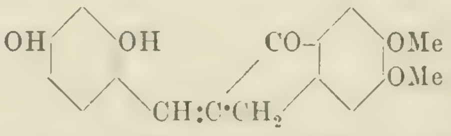
* In this communication, the positions in hydrindene are numbered according to the scheme  .

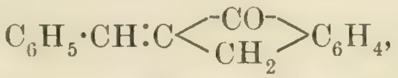
In the condensation products with aldehydes described in this paper the additional benzene ring is distinguished by using the numerals 1′, 2′, 3′, &c., thus the substance



(p. 1097) is 5 : 6-*dimethoxy*-2-*benzylidene*-2′ : 4′-*dihydroxy*-1-*hydrindone.*

it seemed to us that valuable information as to its constitution might be obtained by the synthesis and careful investigation of certain derivatives of this hydrocarbon and by the subsequent condensation of such hydrindene derivatives with aldehydes and especially with *p*-methoxysalicylaldehyde.

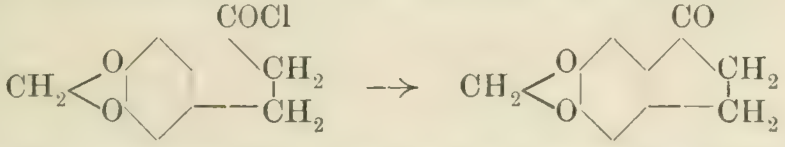
Kipping, during the course of his important researches on hydrindone (Trans., 1894, 65, 498), has shown that 1-hydrindone condenses very readily with benzaldehyde with the formation of 2-benzylidene-1-hydrindone (*β*-benzylidene-*α*-hydrindone),



$$C_6H_5\cdot CH{:}C{<}\begin{matrix}\text{-CO-}\\ CH_2\end{matrix}{>}C_6H_4,$$

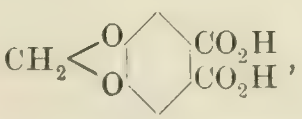
and this observation suggested that the main object of our investigation should be the synthesis of derivatives of 1-hydrindone which then, on reduction, could be converted into the corresponding derivatives of 1-hydroxyhydrindene. It has already been pointed out that the derivative of hydrindone which is of special interest on account of its close relationship to trimethylbrazilin is 5 : 6-dimethoxy-1-hydrindone, and although the synthesis of this substance was ultimately successfully accomplished, a long series of comparative experiments was necessary before it could be obtained in any considerable quantity.

Since one of the principal difficulties encountered was the preparation in sufficient quantities of veratraldehyde, and piperonal is easily accessible, we decided, in the first place, to study the conditions of formation and properties of the substituted hydrindone obtained from the latter aldehyde and to proceed afterwards with the preparation of 5 : 6-dimethoxy-1-hydrindone. Piperonylacrylic acid (methylenecaffeic acid) $CH_2{:}O{:}C_6H_3\cdot CH{:}CH\cdot CO_2H$, was prepared by condensing piperonal with ethyl acetate in the presence of sodium and reduced to piperonylpropionic acid, the chloride of which, when treated with aluminium chloride, yielded 5 : 6-*methylenedioxy*-1-*hydrindone* :



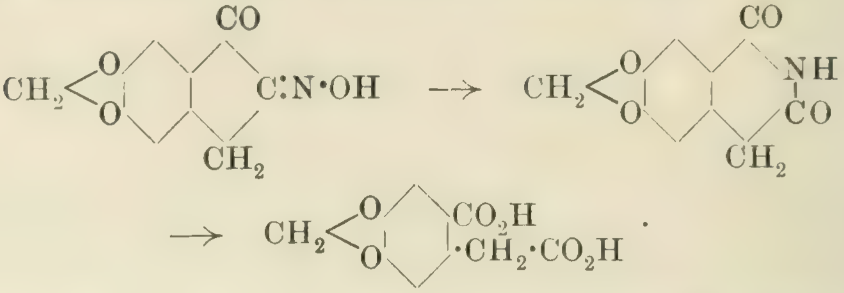
(compare Kipping, *loc. cit.*, 484) and an even better yield of this substance was obtained when the acid itself was treated with phosphoric oxide under the conditions described on p. 1081.

This hydrindone proved to be of interest from several points of view. Thus it is readily oxidised by nitric acid with formation of *hydrastic acid*,

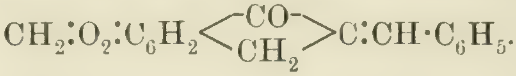


and since hydrastic acid is one of the most important products of the oxidation of hydrastine and berberine, its synthesis in this comparatively simple manner is of considerable interest.

*iso*Amyl nitrite converts methylenedioxyhydrindone into an *isonitroso*-compound which, when treated with phosphorus pentachloride, undergoes the Beckmann rearrangement, and the product, on hydrolysis with potash, yields 2-*carboxy*-4 : 5-*methylenedioxyphenylacetic acid*,

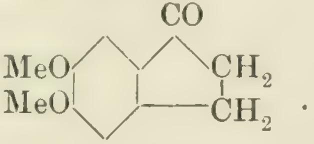


We also found that this hydrindone condenses readily with aldehydes, the product formed, in the case of benzaldehyde, for example, being 5 : 6-*methylenedioxy*-2-*benzylidene*-1-*hydrindone*,

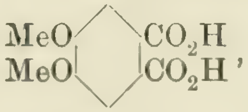


$$CH_2{:}O_2{:}C_6H_2{<}{\overset{-CO-}{\underset{CH_2}{}}}{>}C{:}CH{\cdot}C_6H_5.$$

Having next worked out the most favourable conditions for the preparation of veratraldehyde and 5 : 6-dimethoxyphenylacrylic acid (dimethylcaffeic acid) we converted the latter into 5 : 6-dimethoxypropionic acid by reduction and then, by treatment with phosphoric oxide, into 5 : 6-*dimethoxy*-1-*hydrindone* (p. 1080),

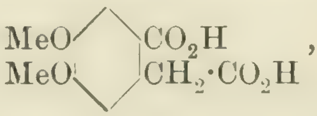


This dimethoxyhydrindone yields m-*hemipinic acid*,



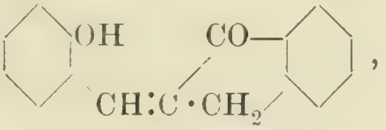
when it is oxidised with nitric acid and this synthesis is not only interesting on account of the importance attaching to *m*-hemipinic acid, but also because the formation of this acid clearly proves that dimethoxyhydrindone contains the two methoxy-groups in the 5 : 6- and not, as might well have been the case, in the 3 : 4-position.

5 : 6-Dimethoxy-1-hydrindone yields an *iso*nitroso-compound and this is readily converted into 2-*carboxy*-4 : 5-*dimethoxyphenylacetic acid*,



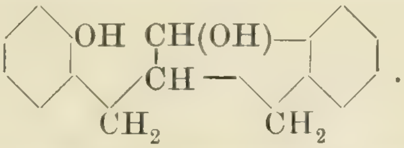
by treatment with phosphorus pentachloride in the manner already described in the case of 5 : 6-methylenedioxy-1-hydrindone.

In studying the condensation of hydrindones with aldehydes we selected, in the first instance, a simple case and investigated carefully the nature of the substances produced when salicylaldehyde condenses with 1-hydrindone. These two substances combine readily in the presence of a trace of alkali with elimination of water and formation of *2′-hydroxy-2-benzylidene-1-hydrindone* (p. 1087):

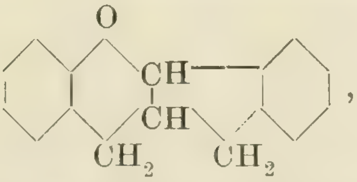


but when hydrochloric acid is employed in the place of the alkali, condensation takes place in a different direction (p. 1090).

Hydroxybenzylidenehydrindone yields crystalline potassium, acetyl, and benzoyl derivatives, and when reduced with sodium amalgam it is converted into *1 : 2′-dihydroxy-2-benzylhydrindene*,

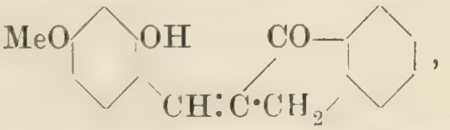


This substance reacts readily with acetyl chloride with elimination of water and formation of *1 : 2-hydrindochroman*,

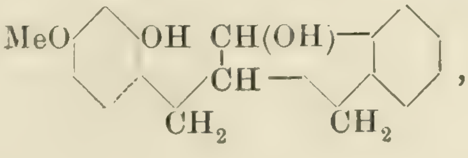


a compound which is of special interest on account of the fact that it is the parent substance from which the formula for trimethylbrazilin, given at the commencement of this paper, is derived.

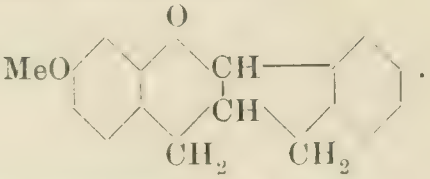
We next investigated the behaviour of *p*-methoxysalicylaldehyde and 1-hydrindone in the presence of alkali and found that, in this case also, condensation takes place readily with formation of *2′-hydroxy-4′-methoxy-2-benzylidene-1-hydrindone* (p. 1091),



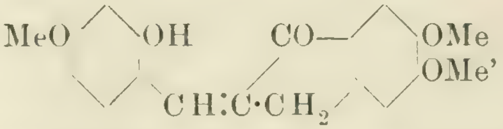
and from this substance we prepared *1 : 2′-dihydroxy-4′-methoxy-2-benzylhydrindene*,



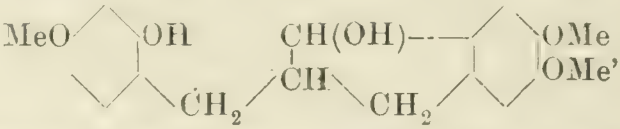
and 4′-*methoxy*-1 : 2-*hydrindochroman*,



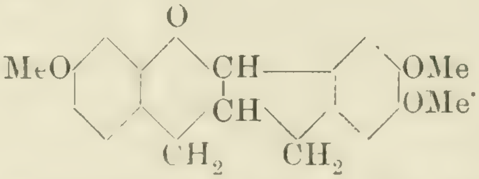
Many other similar condensations, which need not be discussed in this introduction, are described in the experimental part of this paper, and have led to the preparation of a long series of new compounds, some of which will be employed in connexion with experiments on the synthesis of the degradation products of trimethylbrazilin. The results which were obtained during the course of our experiments on the condensation of *p*-methoxysalicylaldehyde with 5 : 6-dimethoxy-1-hydrindone (p. 1098) are, however, of special interest on account of their bearing on the question of the constitution of brazilin. These substances combine readily in the presence of a trace of caustic potash, with formation of 2′-*hydroxy*-4′ : 5 : 6-*trimethoxy*-2-*benzylidene*-1-*hydrindone*.



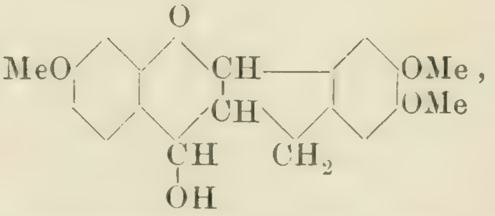
which, when reduced with sodium amalgam, yields 1 : 2′-*dihydroxy*-4′ : 5 : 6-*trimethoxy*-2-*benzylhydrindene*,



and this substance is readily decomposed by boiling with glacial acetic acid with elimination of water and formation of 4′ : 5 : 6-*trimethoxy*-1 : 2-*hydrindochroman*,



The special interest which attaches to this substance lies in the fact that it is so very closely related to the formula for *trimethylbrazilin*,



mentioned at the commencement of this paper, from which indeed dried over calcium chloride, and evaporated. As soon as crystallisation is complete the mass is left in contact with porous porcelain until quite dry, and then twice recrystallised from ether from which the pure substance separates in colourless prisms :

0·2374 gave 0·5980 CO_2 and 0·1310 H_2O. C = 68·7 ; H = 6·1.
$C_{11}H_{12}O_3$ requires C = 68·8 ; H = 6·2 per cent.

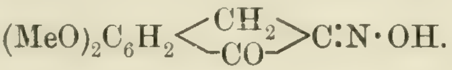
5 : 6-*Dimethoxy*-1-*hydrindone* melts at 115° and is readily soluble in methyl or ethyl alcohol, less so in ether, and almost insoluble in light petroleum. It dissolves in concentrated sulphuric acid with a red colour and is not volatile in steam.

The constitution of this hydrindone is proved by its conversion into *m*-hemipinic acid on oxidation (see p. 1083).

II. *Preparation of* 5 : 6-*Dimethoxy*-1-*hydrindone by the Action of Phosphoric Oxide on* 3 : 4-*Dimethoxyphenylpropionic Acid.*—The yield of this hydrindone obtained by the process just described varies very much and is seldom more than 5 grams and frequently only 1 to 2 grams, and since we required this substance in quantity we instituted a number of comparative experiments and ultimately devised the following process as the most suitable for its preparation. Dimethoxyphenylpropionic acid (40 grams) is dissolved in boiling benzene (300 c.c.), gradually mixed with phosphoric oxide (200 grams), the whole being well shaken after each addition.

After boiling for two to three hours, the product is mixed with ice by which means the bluish-red phosphorus compound is decomposed and a pale yellow solution is obtained. The whole is shaken with a large quantity of ether, washed with dilute potash, dried over calcium chloride, evaporated, and the last traces of benzene removed by passing a current of dry air, when a pale yellow, crystalline mass (30 grams) remains which consists of almost pure 5 : 6-dimethoxy-1-hydrindone.

iso*Nitroso*-5 : 6-*dimethoxy*-1-*hydrindone*,



$$(\mathrm{MeO})_2\mathrm{C_6H_2}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CO}\end{matrix}>\mathrm{C{:}N\cdot OH}.$$

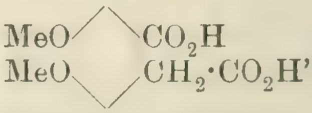
—When dimethoxyhydrindone (5 grams) dissolved in methyl alcohol (15 c.c.) is mixed with freshly distilled *iso*amyl nitrite (7 grams) and hydrochloric acid (3 c.c.) and the mixture maintained at 50° for half an hour, the *iso*nitroso-compound separates in crystals.

After collecting by the aid of the pump, the brownish-yellow, sandy powder is washed with cold alcohol and recrystallised from alcohol or acetic acid, from both of which the substance separates in small, yellow needles. The yield is almost quantitative :

0·5029 gave 24·2 c.c. of nitrogen at N.T.P. N = 6·0.
$C_{11}H_{11}O_4N$ requires N = 6·3 per cent.

iso*Nitroso*-5 : 6-*dimethoxy*-1-*hydrindone* decomposes at about 240° and is soluble in dilute potash, forming a deep yellow solution.

It dissolves in concentrated sulphuric acid with an intense red colour and is precipitated unchanged on dilution with water, a behaviour similar to that shown by benziloxime and oximes of other α-diketones. Like *iso*nitroso-1-hydrindone, the alcoholic solution gives an orange coloration with ferric chloride, which is much deepened on warming but fades again on cooling (compare Kipping, Trans., 1894, **65**, 493).

2-*Carboxy*-4 : 5-*dimethoxyphenylacetic Acid*,  *and* 2-*Carboxyphenylacetic Acid*, $C_6H_4(CO_2H)\cdot CH_2\cdot CO_2H$.

2-Carboxy-4 : 5-dimethoxyphenylacetic acid, which is of special interest on account of its being one of the products obtained when trimethylbrazilin is oxidised with permanganate (Perkin, Trans., 1902, **81**, 1028), may be obtained from dimethoxyhydrindone as follows.

The *iso*nitroso-compound (3 grams) is suspended in ether (20 c.c.) and gradually treated with phosphorus pentachloride (10 grams), when a vigorous reaction sets in and the *iso*nitroso-compound dissolves. After remaining for half an hour, the product is poured in a thin stream into ice water, the ethereal layer separated and evaporated, and the residual oil left in contact with water until decomposition is complete. The brown solid which separates is collected by the aid of the pump and digested with caustic potash (5 grams) and water (25 c.c.) for half an hour and until the evolution of ammonia has ceased. The addition of hydrochloric acid to the alkaline solution causes the separation of crude 2-carboxy-4 : 5-dimethoxyphenylacetic acid as a brown precipitate which after crystallising from water with the aid of animal charcoal is readily obtained colourless :

0·1731 gave 0·3481 CO_2 and 0·0791 H_2O. $C = 54\cdot8$; $H = 5\cdot1$.

$C_{11}H_{12}O_6$ requires $C = 55\cdot0$; $H = 5\cdot0$ per cent.

2-*Carboxy*-4 : 5-*dimethoxyphenylacetic acid* melts at about 215° with decomposition and is identical with the acid obtained from trimethylbrazilin (see above) since an intimate mixture of both specimens melted at 215—216°.

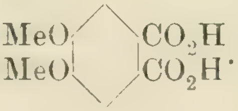
2-*Carboxyphenylacetic acid* (Homophthalic acid) is obtained when *iso*nitroso-1-hydrindone (Kipping, Trans., 1894, **65**, 492) (5 grams) suspended in ether (20 c.c.) is treated with phosphorus pentachloride until solution is complete. The product is poured into water and digested with excess of caustic potash for half an hour, the solution nearly neutralised, boiled with animal charcoal, filtered, and acidified with hydrochloric acid. After recrystallisation from a mixture of ethyl acetate and benzene, colourless crystals are obtained which melt at 175—177° and consist of pure 2-carboxyphenylacetic acid :

0·2142 gave 0·4709 CO_2 and 0·0885 H_2O. C = 60·0 ; H = 4·6.

$C_9H_8O_4$ requires C = 60·0 ; H = 4·4 per cent.

Since the yield of 2-carboxyphenylacetic acid is almost theoretical, the above is probably the most convenient method for the preparation of this acid.

m-*Hemipinic Acid*,



This important acid may be obtained from 5 : 6-dimethoxy-1-hydrindone by the two following methods.

I. *By Oxidation with Nitric Acid.*—When dimethoxyhydrindone (3 grams) is boiled with nitric acid (12 grams) and water (36 c.c.), oxidation takes place readily, and a clear yellow solution is soon formed. This is neutralised with sodium carbonate, mixed with hydrochloric acid until the solution just turns congo-paper blue, evaporated to dryness, and the residue mixed with sand and extracted in a Soxhlet apparatus with ether. The ethereal solution is dried over anhydrous sodium sulphate, evaporated, and the residue dissolved in hot water, digested with animal charcoal, filtered, and the concentrated solution allowed to evaporate slowly in the air, when large, transparent crystals separate which melt at about 179° :

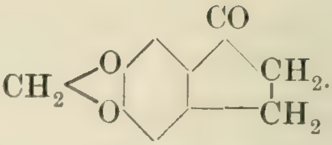
0·1904 gave 0·3287 CO_2 and 0·0943 H_2O. C = 45·6 ; H = 5·3.

$C_{10}H_{10}O_6,2H_2O$ requires C = 45·8 ; H = 5·3 per cent.

That this acid is *m*-hemipinic acid was proved by conversion into the characteristic ethylimide which melted at 228° (compare Goldschmiedt, *Monatsh.*, 1888, **9**, 775).

II. *From* iso*Nitrosodimethoxyhydrindone by Oxidation with Permanganate.*—The *iso*nitroso-compound is dissolved in dilute caustic potash and then a cold saturated solution of potassium permanganate is gradually added until the pink colour remains, even after gently warming on the water-bath. The excess of permanganate is destroyed by the addition of sodium bisulphite, the filtrate and washings from the manganese precipitate evaporated to a small bulk, acidified, saturated with ammonium sulphate, and extracted several times with ether. The residue obtained on evaporating the ethereal solution is crystallised from water, when pale yellow crystals of *m*-hemipinic acid separate, the yield being almost theoretical.

5 : 6-*Methylenedioxy*-1-*hydrindone*,



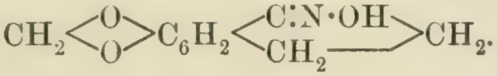
The methylenedioxycinnamic acid, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$, required for the synthesis of the above ketone, had already been prepared by Reychler (*Bull. Soc. chim.*, 1897, [iii], **17**, 515) by condensing piperonal with ethyl acetate in the presence of sodium. The conditions we employed in its preparation were the same as those described in the corresponding preparation of dimethoxycinnamic acid (p. 1079) and the quantities used in each preparation were: piperonal (100 grams), ethyl acetate (180 grams) and sodium (18 grams). The ester obtained in this way was hydrolysed by a methyl-alcoholic solution of caustic potash in the usual manner and the alkaline solution, after removal of the alcohols by evaporation, was nearly neutralised and reduced by sodium amalgam, care being taken to keep the solution only slightly alkaline during the operation (compare p. 1080). After acidifying and recrystallising from benzene, the piperonylpropionic acid melted at 87—88°, and not at 85° as stated by Lorenz (*Ber.*, 1880, **13**, 758) who also observed that the acid dissolves in sulphuric acid with a cherry-red colour, a reaction which is doubtless due to the formation of 5 : 6-methylenedioxy-1-hydrindone. The latter substance may be readily obtained from piperonylpropionic acid by either of the methods recommended for the preparation of 5 : 6-dimethoxy-1-hydrindone from 3 : 4-dimethoxyphenylpropionic acid (pp. 1080–1), but the yield obtained when the aluminium chloride method is employed is only about 15 per cent. of that theoretically possible. On the other hand, the action of phosphoric oxide (100 grams) on the benzene (100 c.c.) solution of the acid (20 grams) gives an almost quantitative yield of methylenedioxyhydrindone, since in one experiment, carried out exactly under the conditions described on p. 1081, 8 grams of ketone were obtained from 10 grams of acid and, at the same time, a small quantity of unchanged acid was recovered.

5 : 6-*Methylenedioxy*-1-*hydrindone* separates from ether, in which it is readily soluble, in colourless prisms and melts at 160°:

0·3189 gave 0·7964 CO_2 and 0·1317 H_2O. C = 68·1; H = 4·6.
$C_{10}H_8O_3$ requires C = 68·1; H = 4·5 per cent.

It is readily soluble in alcohol, acetic acid, ethyl acetate, or boiling benzene, but sparingly so in light petroleum, and crystallises readily from almost all solvents. It dissolves in sulphuric acid with a cherry-red colour. When it is boiled with dilute sulphuric acid it dissolves, and the solution becomes orange and then red, and, if cooled at this stage, a red solid is obtained; if, however, the boiling is continued, a blue substance is produced.

5 : 6-*Methylenedioxy*-1-*hydrindoneoxime*,



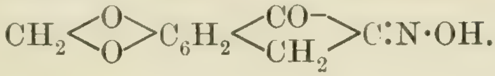
$$CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}C{:}N\cdot OH\\CH_2\end{matrix}\right>CH_2.$$

This substance is readily obtained when the hydrindone, dissolved in methyl alcohol, is treated with hydroxylamine hydrochloride and caustic potash in the usual manner. It separates from methyl alcohol in prisms and decomposes at about 246°:

0·3727 gave 22·3 c.c. nitrogen at N.T.P. N = 7·5

$C_{10}H_9O_3N$ requires N = 7·3 per cent.

iso*Nitroso*-5 : 6-*methylenedioxy*-1-*hydrindone*,



$$CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}CO-\\CH_2\end{matrix}\right>C{:}N\cdot OH.$$

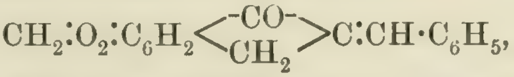
In preparing this characteristic derivative, the hydrindone (10 grams) is dissolved in boiling methyl alcohol (30 c.c.), mixed with *iso*amyl nitrite (15 grams) and hydrochloric acid (5 c.c.) and the solution kept at 50° for one hour. The crystals of the *iso*nitroso-compound, which separate in an almost quantitative yield, are collected by the aid of the pump, washed with cold alcohol, and purified by recrystallisation from alcohol, from which the substance separates in yellow needles, which decompose at about 230°:

0·5008 gave 25·6 c.c. nitrogen at N.T.P. N = 6·4.

$C_{10}H_7O_4N$ requires N = 6·8 per cent.

This *iso*nitroso-compound behaves towards alkalis, sulphuric acid, and ferric chloride in the same way as *iso*nitroso-5 : 6-dimethoxy-1-hydrindone (p. 1082).

5 : 6-*Methylenedioxy*-2-*benzylidene*-1-*hydrindone*,



$$CH_2{:}O_2{:}C_6H_2\left<\begin{matrix}-CO-\\CH_2\end{matrix}\right>C{:}CH\cdot C_6H_5,$$

is readily obtained when the hydrindone (2 grams), dissolved in freshly distilled benzaldehyde (3 grams) and a little alcohol, is treated with two or three drops of concentrated alcoholic potash.

After warming gently, the mixture crystallises and the product is collected by the aid of the pump, washed with alcohol and then with water and recrystallised from alcohol, from which it separates in yellow prisms of melting point 200°:

0·2052 gave 0·5796 CO_2 and 0·0850 H_2O. C = 77·0; H = 4·6

$C_{17}H_{12}O_3$ requires C = 77·3; H = 4·5 per cent.

2-Carboxy-4 : 5-methylenedioxyphenylacetic Acid, $CH_2:O_2:C_6H_2(CO_2H)CH_2\cdot CO_2H$, *and Hydrastic Acid,* $CH_2:O_2:C_6H_2(CO_2H)_2$.

When *iso*nitroso-5 : 6-methylenedioxy-1-hydrindone (5 grams) is covered with dry ether and treated with phosphorus pentachloride until no further action takes place, a clear solution is obtained, which, when treated with water, yields a brown precipitate.

This was collected and digested with caustic potash until the evolution of ammonia had ceased; hydrochloric acid was then added, and the acid, which separated in needles, collected and purified by recrystallisation from water:

0·3430 gave 0·6728 CO_2 and 0·1136 H_2O. C = 53·5; H = 3·7.
$C_{10}H_8O_6$ requires C = 53·6; H = 3·6 per cent.

2-Carboxy-4 : 5-methylenedioxyphenylacetic acid crystallises from water in colourless needles, and melts at about 236° with decomposition.

Hydrastic Acid.—This important acid is readily obtained from 5 : 6-methylenedioxy-1-hydrindone by oxidation with nitric acid under the following conditions. The hydrindone (5 grams) is digested with nitric acid (20 grams) and water (60 c.c.) for four hours, when on cooling an apparently amorphous precipitate separates.

After neutralising with caustic potash, hydrochloric acid is added until congo-paper is just turned blue, the solution is evaporated to dryness and extracted in a Soxhlet apparatus with ether. The ethereal solution deposits on evaporation a brown, crystalline mass, which, after repeated recrystallisation from water with the aid of animal charcoal, is obtained in colourless needles:

0·1469 gave 0·2762 CO_2 and 0·0372 H_2O. C = 51·3; H = 2·8.
$C_9H_6O_6$ requires C = 51·4; H = 2·9 per cent.

When slowly heated this acid melted at 172°, but, when the operation was quickly conducted, at 188°, and it yielded a sparingly soluble calcium salt. These and other properties prove conclusively that the acid is *hydrastic acid*, identical with the hydrastic acid obtained from berberine or hydrastine by oxidation with permanganate (Perkin, Trans., 1890, 57, 1095*; Freund, *Annalen*, 1892, 271, 375).

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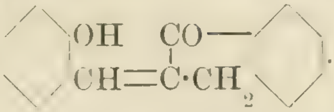
[*] The position of the methylenedioxy-group is incorrectly given in this and in several other of the formulæ printed in this communication.

Condensation of Salicylaldehyde with 1-*Hydrindone. Formation of* 2′-*Hydroxy*-2-*benzylidene* 1-*hydrindone*,



This condensation takes place readily when a mixture of 1-hydrindone (10 grams) and salicylaldehyde (10 grams) is treated with a solution of caustic potash (4 grams) in methyl alcohol (50 c.c.) and heated to boiling for twenty minutes. The product is acidified with acetic acid, diluted with water, and the bright canary-yellow precipitate collected, washed with water, and recrystallised from alcohol:

0·1803 gave 0·5391 CO_2 and 0·0824 H_2O. C = 81·5; H = 5·1.

$C_{16}H_{12}O_2$ requires C = 81·4; H = 5·1 per cent.

2′-*Hydroxy*-2-*benzylidene*-1-*hydrindone* melts at 206° with decomposition and is sparingly soluble in cold alcohol but separates when its solution in boiling alcohol is allowed to cool slowly in slender, canary yellow needles. The alcoholic solution gives a yellow coloration with ferric chloride, and the hydrindone dissolves in concentrated sulphuric acid to a yellow solution which when gently warmed acquires a violet fluorescence.

When heated in a sealed tube with water at 150° for twenty-four hours it is decomposed by hydrolysis into salicylaldehyde and 1-hydrindone.

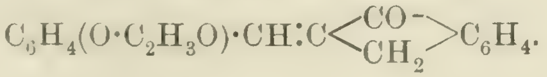
The *potassium* derivative separates in splendid red crystals with a green reflex when the hydrindone is dissolved in hot alcoholic potash and the solution diluted with water and allowed to cool slowly. For analysis the substance was dried at 100°:

0·3016 gave 0·0955 K_2SO_4. K = 14·2.

$C_{16}H_{11}O_2K$ requires K = 14·2 per cent.

This potassium derivative also separates in an almost pure condition when the alkaline product of the condensation of salicylaldehyde and 1-hydrindone, obtained as explained above, is allowed to cool slowly. It is sparingly soluble in alcohol or water; the dilute solutions are yellow, whilst the concentrated solutions are red.

2′-*Acetoxy*-2-*benzylidene*-1-*hydrindone*,



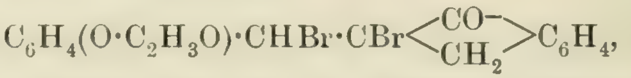
$$C_6H_4(O{\cdot}C_2H_3O){\cdot}CH{:}C{<}{\substack{CO-\\CH_2}}{>}C_6H_4.$$

This substance is readily produced by the action of acetic anhydride and sodium acetate on salicylidene-1-hydrindone, but it is most conveniently prepared from the potassium derivative. This derivative (5 grams) is heated on the water-bath with acetic anhydride (20 c.c.)

for five minutes, the product decomposed by water and the precipitate collected, washed with water, and crystallised from alcohol:

0·2188 gave 0·6223 CO_2 and 0·1014 H_2O. C = 77·6; H = 5·1.
$C_{18}H_{14}O_3$ requires C = 77·7; H = 5·0 per cent.

2′-*Acetoxy-2-benzylidene-1-hydrindone* separates from alcohol in almost colourless needles and melts at 150°.

The *dibromide*,  $C_6H_4(O\cdot C_2H_3O)\cdot CHBr\cdot CBr\Big<{CO-\atop CH_2}\Big>C_6H_4$, was prepared by adding a solution of bromine (3 grams) in carbon disulphide to the acetyl compound dissolved in the least possible quantity of the same solvent. The product was left exposed to the air, and as the carbon disulphide evaporated, long, prismatic needles separated which were collected and recrystallised from alcohol, from which the dibromide was deposited in stout, colourless needles melting at 159°:

0·1970 gave 0·1678 AgBr. Br = 36·2.
$C_{18}H_{14}O_3Br_2$ requires Br = 36·5 per cent.

The action of zinc dust and acetic acid on this dibromide was carefully investigated in the hope of replacing the bromine atom by hydrogen, but the experiments always yielded amorphous substances which were not further examined.

2′-*Benzoxy-2-benzylidene-1-hydrindone* is readily obtained when a solution of the hydrindone in excess of caustic soda is shaken with benzoyl chloride in the usual manner. It separates from alcohol in pale yellow needles and melts at 149°:

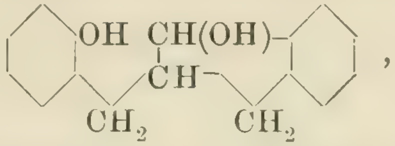
0·1519 gave 0·4512 CO_2 and 0·0652 H_2O. C = 81·0; H = 4·8.
$C_{23}H_{16}O_3$ requires C = 81·2; H = 4·7 per cent.

2′-*Hydroxy-2-benzylidene-1-hydrindone* undergoes a remarkable decomposition into the oximes of salicylaldehyde and 1-hydrindone when it is treated with hydroxylamine hydrochloride and caustic potash in the usual manner. The pale yellow solution was acidified with acetic acid and the precipitate crystallised from alcohol, when colourless needles were obtained which melted at 146° and consisted of the oxime of 1-hydrindone. The acetic acid mother liquor was allowed to concentrate in a vacuum desiccator, when crystals separated which, after recrystallisation from benzene, melted at 56° and consisted of salicylaldoxime. Evidently, under the conditions employed, salicylidene-1-hydrindone is decomposed by hydrolysis into salicylaldehyde and 1-hydrindone, which then combine with the hydroxylamine and are converted into their oximes, but it is remarkable that this hydrolysis should take place so readily and in the presence of caustic potash.

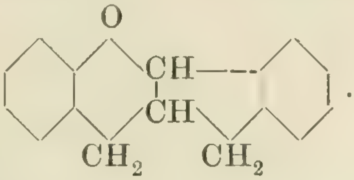
2′-*Hydroxybenzylidene-1-hydrindonesulphonic Acid.*—When 2′-hydroxybenzylidene-1-hydrindone is dissolved in sulphuric acid an orange solution is obtained which fades considerably on standing, and water then precipitates a gelatinous yellowish-brown precipitate of a sulphonic acid. This was collected, dissolved in excess of aqueous alcoholic potash, and hydrochloric acid added to the deep orange solution until the colour became only yellow when a yellow precipitate of the potassium salt separated which crystallised from alcohol in slender needles containing solvent of crystallisation. After drying in the water oven, the following results were obtained on analysis:

0·1987 gave 0·1254 $BaSO_4$. S = 8·6.
0·1319 ,, 0·0321 K_2SO_4. K = 10·9.
$C_{16}H_{11}O_2{\cdot}SO_3K$ requires S = 9·0; K = 11·0 per cent.

1 : 2′-*Dihydroxy-2-benzylhydrindene*,



and its Conversion into 1 : 2-*Hydrindochroman*,



1 : 2′-Dihydroxy-2-benzylhydrindene is produced when 2′-hydroxy 2-benzylidene-1-hydrindone is reduced with sodium amalgam (compare C. Harries and G. Busse, *Ber.*, 1896, **29**, 375).

2′-*Hydroxy*-2-*benzylidene*-1-*hydrindone* (5 grams) is dissolved in methyl alcohol (50 c.c.) and caustic potash (2 grams), diluted with water (200 c.c.), and treated with sodium amalgam * (200 grams of 3 per cent.) in an apparatus fitted with a mechanical stirrer, any considerable excess of alkali being neutralised from time to time by the careful addition of hydrochloric acid. After one hour, a further quantity of sodium amalgam (100 grams) is added and the same quantity again after the second hour. The product is acidified with hydrochloric acid, extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil left to crystallise and then transferred to porous porcelain. When quite free from oily impurity, the crystalline mass is dissolved in ether, digested with animal charcoal, the ethereal solution carefully dried and evaporated to a small bulk, when the new substance gradually separates in minute balls of needles. After recrystallisation, the following results were obtained on analysis:

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* It is most important in this and other similar reductions (pp. 1902-6, 1100) that the sodium amalgam employed is prepared from perfectly clean mercury and sodium, otherwise resinous products are obtained which it is almost impossible to purify.

0·1076 gave 0·3152 CO_2 and 0·0654 H_2O. C = 79·9 ; H = 6·7.

$C_{16}H_{16}O_2$ requires C = 80·0 ; H = 6·7 per cent.

1 : 2′-*Dihydroxy-2-benzylhydrindene* melts at 143° and is readily soluble in most organic solvents. Its conversion into 1 : 2-hydrindochroman may be readily carried out under the following conditions.

The substance (2 grams) is digested with acetyl chloride (10 c.c.) for ten minutes, the acetyl chloride and acetic acid are then distilled off from the water-bath under 20 mm. pressure, and the residue digested for a few minutes with caustic potash (3 grams) dissolved in methyl alcohol. The product is diluted with water and left in the ice-chest overnight, the solid which will then have been deposited is collected by the aid of the pump and crystallised from alcohol. The yield is 1·5 grams:

0·1214 gave 0·3839 CO_2 and 0·0698 H_2O. C = 86·2 ; H = 6·4.

$C_{16}H_{14}O$ requires C = 86·5 ; H = 6·3 per cent.

2 : 3-*Hydrindochroman* also appears to be formed when dihydroxybenzylhydrindene is digested for a few minutes with glacial acetic acid. It separates from alcohol in small prisms, melts at 61°, and appears to sublime at the ordinary temperature. It has a pleasant, sweet odour, is insoluble in boiling caustic potash, and dissolves in sulphuric acid, forming a colourless solution. The interest attaching to this substance, owing to its close relationship to brazilin and hæmatoxylin, is emphasised in the introduction to this paper (p. 1077).

It has just been shown (p. 1087) that salicylaldehyde condenses with 1-hydrindone in the presence of caustic potash with the formation of 2′-hydroxy-2-benzylidene-1-hydrindone. When, however, hydrochloric acid is employed in the place of caustic potash, the condensation proceeds in another direction. Salicylaldehyde (2 grams) and 1-hydrindone (2 grams) are dissolved in alcohol (35 c.c.), mixed with concentrated hydrochloric acid (30 c.c.) and water (30 c.c.), and allowed to remain at the ordinary temperature for three weeks.

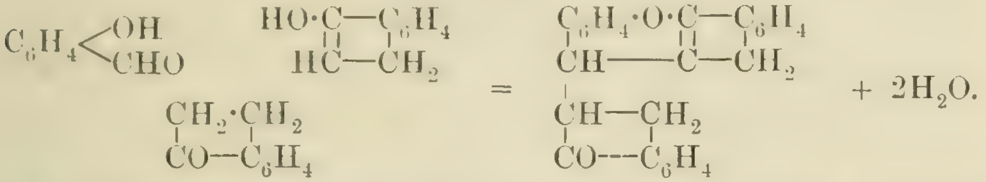
The orange solution deposits a large quantity of crystals, which are collected, washed with warm alcohol, and recrystallised from much boiling alcohol in which the substance is very sparingly soluble:

0·1514 gave 0·4731 CO_2 and 0·0675 H_2O. C = 85·2 ; H = 4·9.
0·1978 ,, 0·6192 CO_2 ,, 0·0857 H_2O. C = 85·4 ; H = 4·8.

$C_{25}H_{18}O_2$ requires C = 85·7 ; H = 5·1 per cent.

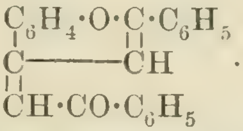
This substance separates from alcohol in glistening, yellow needles, melts at 206°, and dissolves in concentrated sulphuric acid to a yellow solution which exhibits an intense blue fluorescence.

Although the analytical results are not so sharp as could be wished, there can be little doubt that this condensation product is produced from one molecule of salicylaldehyde and two molecules of 1-hydrindone by the elimination of two molecules of water:



$$C_6H_4\begin{cases}OH\\CHO\end{cases}\quad \begin{array}{l}HO{\cdot}C{-}C_6H_4\\ HC{-}CH_2\\ CH_2{\cdot}CH_2\\ CO{-}C_6H_4\end{array} = \begin{array}{l}C_6H_4{\cdot}O{\cdot}C{-}C_6H_4\\ CH{-\!-}C{-}CH_2\\ CH{-}CH_2\\ CO{-}C_6H_4\end{array} + 2H_2O.$$

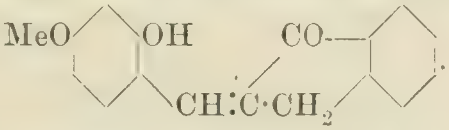
A similar substance had been obtained by Feuerstein and Kostanecki (*Ber.*, 1898, **31**, 711) from 2'-hydroxybenzylidenediacetophenone, $OH{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}CO{\cdot}C_6H_5)_2$ (the product of the condensation of one molecule of salicylaldehyde with two molecules of acetophenone) by treatment with hydrochloric acid. The substance produced had, however, the formula $C_{23}H_{16}O_2$ instead of $C_{23}H_{18}O_2$, which would normally result from the elimination of water, and it was therefore assumed that two hydrogen atoms have been removed during the process of condensation and that the condensation product had the formula:



$$\begin{array}{l}C_6H_4{\cdot}O{\cdot}C{\cdot}C_6H_5\\ C{-\!-\!-}CH\\ CH{\cdot}CO{\cdot}C_6H_5\end{array}.$$

Like the condensation product from salicylaldehyde and 1-hydrindone, the substance $C_{23}H_{16}O_2$ is yellow, and the yellow solution in sulphuric acid also exhibits a blue fluorescence.

2'-*Hydroxy*-4'-*methoxy*-2-*benzylidene*-1-*hydrindone*,



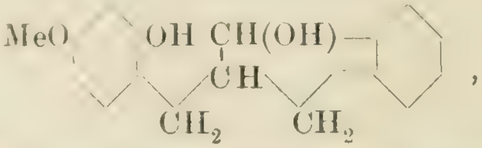
In order to prepare this substance, *p*-methoxysalicylaldehyde (5 grams) and 1-hydrindone (5 grams) are digested for one hour with caustic potash (5 grams) dissolved in methyl alcohol. The deep red solution is acidified with dilute acetic acid, the precipitate collected, washed with water, and crystallised from alcohol, from which 2'-*hydroxy*-4'-*methoxy*-2-*benzylidene*-1-*hydrindone* separates in bright yellow needles and melts at about 220° with decomposition:

0·2111 gave 0·5926 CO_2 and 0·1028 H_2O. C = 76·6; H = 5·4.
$C_{17}H_{14}O_3$ requires C = 76·7; H = 5·2 per cent.

The *acetyl* derivative, obtained by digesting with acetic anhydride and anhydrous sodium acetate (*cf.* p. 1087), crystallises from alcohol in pale yellow needles and melts at 155°:

0·1547 gave 0·4187 CO_2 and 0·0728 H_2O. C = 73·8; H = 5·2.
$C_{19}H_{16}O_4$ requires C = 74·0; H = 5·2 per cent.

1 : 2′-*Dihydroxy-4′-methoxy-2-benzylhydrindene*,



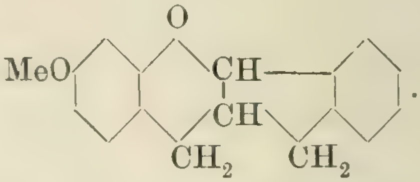
is produced when 2′-hydroxy-4′-methoxy-2-benzylidene-1-hydrindone is reduced by sodium amalgam, the conditions employed being exactly the same as those described in detail in the case of 1 : 2′-dihydroxy-2-benzylhydrindene (p. 1089)

The product is acidified with acetic acid and the colourless precipitates collected and recrystallised from ether, from which the dihydroxy-compound separates in needles melting at 152—154°.

0·1482 gave 0·4088 CO_2 and 0·0874 H_2O. C = 75·2 ; H = 6·5.

$C_{17}H_{18}O_3$ requires C = 75·6 ; H = 6·6 per cent.

1 : 2-*Hydrindo*-4′-*methoxychroman*,



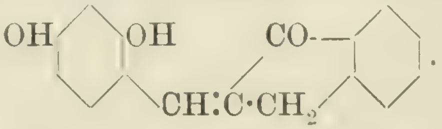
This substance was obtained when 1 : 2′-dihydroxy-4′-methoxy-2-benzylhydrindene was boiled for ten minutes with glacial acetic acid. The product was poured into excess of cold dilute potash and the oil which separated extracted with pure ether, the ethereal solution was washed with dilute potash, then with water, dried over calcium chloride, evaporated, and the residue left for twenty-four hours in a vacuum desiccator.

0·2357 gave 0·6911 CO_2 and 0·1390 H_2O. C = 80·0 ; H = 6·5.

$C_{17}H_{16}O_2$ requires C = 81·0 ; H = 6·3 per cent.

The compound is a thick syrup which, when left in contact with ice-water, gradually solidifies, but it could not be recrystallised ; it does not dissolve even when boiled with dilute caustic potash.

2′ : 4′-*Dihydroxy*-2-*benzylidene*-1-*hydrindone*,



The condensation of 1-hydrindone with benzaldehyde, salicylaldehyde, and *p*-methoxysalicylaldehyde, in presence of alkali, proceeds almost quantitatively but, in the case of *p*-hydroxysalicylaldehyde (β-resorcylaldehyde), although condensation does take place under the same conditions, the yield of condensation product is very small. As we wished to study the properties of this interesting substance in some detail, we were therefore obliged to devise a different method of preparation, and ultimately we found the following process to give good results. β-Resorcylaldehyde (5 grams) and 1-hydrindone (5 grams) are dissolved in glacial acetic acid (25 c.c.) and, after cooling in ice-water, a saturated solution of hydrogen chloride in acetic acid (25 c.c.) is gradually added and a slow stream of hydrogen chloride is then passed for two hours.

The red precipitate which separates is usually amorphous; it is collected and warmed with water when it is decomposed into hydrochloric acid and the hydrindone, the orange precipitate is then crystallised from methyl alcohol and dried at 100°:

0·1456 gave 0·4058 CO_2 and 0·0615 H_2O. C = 76·0; H = 4·7.

$C_{16}H_{12}O_3$ requires C = 76·2; H = 4·7 per cent.

2′ : 4′-*Dihydroxy*-2-*benzylidene*-1-*hydrindone* darkens at 180° and decomposes rapidly at 210°, it separates from methyl alcohol in orange brown plates and dissolves in caustic potash with a purple red colour. Sulphuric acid dissolves it with a yellow colour and, on carefully heating the solution, it acquires a beautiful green fluorescence.

* *The hydrochloride.*—The red precipitate produced when β-resorcylaldehyde condenses with 1-hydrindone, under the conditions described above, is usually amorphous but, on one occasion, it separated in dark red crystals. These were collected, dried on porous porcelain over sulphuric acid, and found to consist of the hydrochloride of the condensation product.

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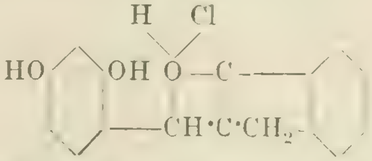
* The constitution of this ketone hydrochloride (and of the other similar hydrochlorides described in this paper, pp. 1095–9, 1102) is not very clear. The simplest assumption is that hydrogen chloride is added to the ·CO· forming a kind of oxonium salt containing the grouping C·C:O(HCl)·C, but this does not appear to account for the brilliant red colour of these hydrochlorides, and it is probable that some more complicated change takes place during their formation.

It is quite conceivable that the hydrochloride of 2′ : 4′-dihydroxy-2-benzylidene-1-hydrindone, for example, may have the constitution:

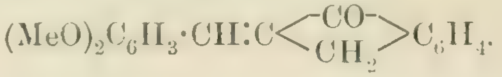


The influence of methoxy-groups on the property of forming hydrochlorides is very striking. 2′-Hydroxy-2-benzylidene-1-hydrindone does not react with hydrochloric acid, the corresponding 2-methoxy-derivative is, however, coloured slightly yellow by concentrated hydrochloric acid. When one hydroxy- and one methoxy-group (or even two of each) are present, the substance forms a red crystalline hydrochloride only with difficulty, and the salt is readily decomposed by cold water. The ketone, $MeO\cdot(OH)C_6H_3\cdot CH{:}C{<}\begin{matrix}CO\\CH_2\end{matrix}{>}C_6H_2(OMe)_2$ (p. 1098), on the other hand, yields a red crystalline hydrochloride, even in dilute aqueous solution, which is so stable that it is decomposed only with difficulty even by much water.

0·2203 gave 0·1064 AgCl. Cl = 11·8.

$C_{16}H_{12}O_3,HCl$ requires Cl = 12·2 per cent.

2′ : 4′-*Dimethoxy*-2-*benzylidene*-1-*hydrindone*,



$$(MeO)_2C_6H_3\cdot CH{:}C\!<\!\begin{matrix}CO\\CH_2\end{matrix}\!>\!C_6H_4.$$

This substance has been obtained in two different ways.

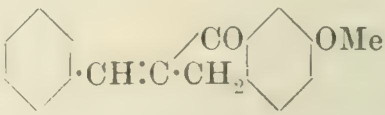
I. *By the methylation of* 2′ : 4′-*dihydroxy*-2-*benzylidene*-1-*hydrindone*.—The hydrindone (1 gram) was dissolved in excess of aqueous caustic potash and vigorously shaken with methyl sulphate (10 grams) the whole being well cooled during the operation and kept alkaline by the addition of small quantities of caustic potash. The original purple red colour gradually changes to yellow, and a solid separates which is collected, washed well, and recrystallised from methyl alcohol, from which it separates in characteristic silky yellow threads which contain methyl alcohol. From ethyl alcohol the substance is obtained in prisms which do not contain alcohol of crystallisation. The 2′ : 4′-dimethoxy-2-benzylidene-1-hydrindone thus obtained melts at 127° and its identity with the substance obtained by Method II was proved by mixing equal quantities of the two preparations, when no alteration in melting point could be observed. The yield obtained is good but, when large quantities are required, the method of preparation is not so convenient as that which follows.

II. *By the condensation of* 2 : 4-*dimethoxybenzaldehyde with* 1-*hydrindone*.—Equal weights of these two substances are dissolved in alcohol and mixed with a few drops of concentrated caustic potash, when condensation rapidly takes place and the mass becomes semi-solid. The precipitate is collected, washed with alcohol and crystallised from the same solvent, when yellow prisms are obtained which melt at 127° and consist of pure 2′ : 4′-*dimethoxy*-2-*benzylidene*-1-*hydrindone* :

0·1790 gave 0·5056 CO_2 and 0·0933 H_2O. C = 77·0 ; H = 5·8.

$C_{18}H_{16}O_3$ requires C = 77·1 ; H = 5·7 per cent.

6-*Methoxy*-2-*benzylidene*-1-*hydrindone*,

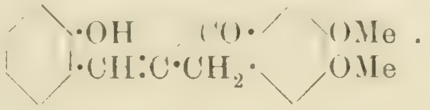


6-Methoxy-1-hydrindone is not formed in appreciable amount when *p*-methoxy-β-phenylpropionic acid is treated with phosphorus pentachloride and then with aluminium chloride. It is, however, produced in small quantities when the acid, dissolved in benzene, is treated with phosphoric oxide under the conditions described in detail in the preparation of 5 : 6-dimethoxy-1-hydrindone (p. 1081).

The hydrindone was not isolated but was, at once, converted into its benzylidene derivative by condensation, in alcoholic solution, with benzaldehyde in the presence of caustic potash. The precipitate was collected and recrystallised from alcohol from which 6-*methoxy*-2-*benzylidene*-1-*hydrindone* separated in yellow needles melting at 134°:

0·1174 gave 0·3503 CO_2 and 0·0600 H_2O. C = 81·4; H = 5·7.
$C_{17}H_{14}O_2$ requires C = 81·6; H = 5·6 per cent.

2′-*Hydroxy*-5 : 6-*dimethoxy*-2-*benzylidene*-1-*hydrindone*,



In the preparation of this substance, salicylaldehyde (5 grams) and 5 : 6-dimethoxyhydrindone (5 grams) are dissolved in alcohol, mixed with concentrated caustic potash (5 grams) and digested for fifteen minutes in a reflux apparatus. The red solution is acidified with acetic acid, the yellow precipitate collected, washed well with cold alcohol, and crystallised from boiling alcohol:

0·1557 gave 0·4145 CO_2 and 0·0738 H_2O. C = 72·6; H = 5·3.
$C_{18}H_{16}O_4$ requires C = 72·9; H = 5·4 per cent.

2′-*Hydroxy*-5 : 6-*dimethoxy*-2-*benzylidene*-1-*hydrindone* separates from alcohol in yellow needles which begin to decompose at 211° and melt with rapid decomposition at 225°. It dissolves in alkalis and in concentrated sulphuric acid yielding yellow solutions.

The *potassium* derivative is obtained when the substance, suspended in boiling alcohol, is mixed with concentrated aqueous potash until a clear solution is produced. The addition of hot water causes the potassium derivative to separate in brick red needles which, after washing with water and drying over sulphuric acid in a vacuum desiccator, gave the following results on analysis:

0·2511 gave 0·0634 K_2SO_4. K = 11·3.
$C_{18}H_{15}O_4K$ requires K = 11·6.

The *hydrochloride* separates in brick-red needles when the solution of the hydroxy-compound in alcohol is saturated with hydrogen chloride. It was collected and rapidly dried on porous porcelain over solid potash in a vacuum desiccator:

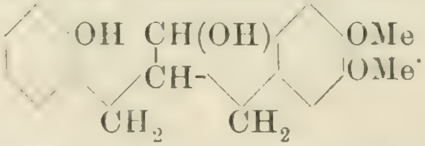
0·1961 gave 0·0815 AgCl. Cl = 10·1.
$C_{18}H_{16}O_4$ HCl requires Cl = 10·5 per cent.

This hydrochloride loses hydrogen chloride if allowed to remain for several days over potash in a vacuum desiccator, and in contact with water it is slowly decomposed into its constituents.

The *acetyl* derivative is readily prepared by digesting the hydroxyketone with acetic anhydride and a little sodium acetate for about ten minutes. The product is poured into water, the precipitate collected and crystallised from alcohol from which the acetate separates in very pale yellow needles melting at 180° :

0·1837 gave 0·4787 CO_2 and 0·0887 H_2O. C = 71·1 ; H = 5·3.
$C_{20}H_{18}O_5$ requires C = 71·0 ; H = 5·3 per cent.

1 : 2′-*Dihydroxy*-5 : 6-*dimethoxy-2-benzylhydrindene*,

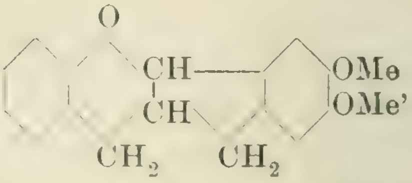


In preparing this substance, 2′-hydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone is dissolved in warm dilute caustic potash and treated with a large excess of 3 per cent. sodium amalgam (compare footnote, p. 1089), acetic acid being added every two or three minutes in such a way that the liquid just remains alkaline. The solution, which at first is deep yellow, gradually becomes nearly colourless, and after then remaining in contact with the sodium amalgam for an hour the whole is acidified with acetic acid, the colourless precipitate collected by the aid of the pump and left in contact with porous porcelain until quite dry. The residue is dissolved in ether, the ethereal solution digested with carefully purified animal charcoal and poured into light petroleum when, on standing, colourless, feathery needles separate which melt indefinitely at about 130° :

0·0990 gave 0·2607 CO_2 and 0·0594 H_2O. C = 71·8 ; H = 6·7.
$C_{18}H_{20}O_4$ requires C = 72·0 ; H = 6·7 per cent.

This substance is readily soluble in ether, alcohol, or chloroform, but sparingly so in light petroleum ; it is, unfortunately, a substance which crystallises only with difficulty. It dissolves readily in alkalis, yielding colourless solutions.

5 : 6-*Dimethoxy*-1 : 2-*hydrindochroman*,



is obtained when the above dihydroxy-compound is boiled with acetic acid for half an hour and separates when the product is poured into excess of dilute potash as an oil which soon solidifies, especially if it is left in contact with several fresh quantities of ice water.

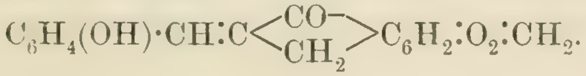
The precipitate was collected, dissolved in chloroform, and precipitated with light petroleum, and after this process had been several times repeated it was dissolved in hot chloroform and hot light petroleum added until a slight turbidity ensued, when, on standing, the substance separated in flocks which, under the microscope, were seen to consist of masses of minute needles:

0·1020 gave 0·2846 CO_2 and 0·1020 H_2O. C = 76·1; H = 6·6.

$C_{18}H_{18}O_3$ requires C = 76·6; H = 6·4 per cent.

5 : 6-*Dimethoxy*-1 : 2-*hydrindochroman* has no definite melting point, it shrinks at 110°, and is melted at about 120°. It is readily soluble in alcohol, benzene, or chloroform, but sparingly so in light petroleum, and it is quite insoluble in caustic potash solution.

2′-*Hydroxy*-5 : 6-*methylenedioxy*-2-*benzylidene*-1-*hydrindone*,



$$C_6H_4(OH)\cdot CH{:}C\begin{matrix}<\\ \end{matrix}\begin{matrix}CO-\\ CH_2\end{matrix}\begin{matrix}>\\ \end{matrix}C_6H_2{:}O_2{:}CH_2.$$

In preparing this substance, salicylaldehyde (6 grams) and 5 : 6-methylenedioxyhydrindone (p. 1084, 9 grams) were dissolved in alcohol (150 c.c.), mixed with a concentrated aqueous solution of caustic potash (4 grams) and boiled for thirty minutes. The red solution was acidified with acetic acid, the yellow precipitate collected and recrystallised from much alcohol, from which it separated in bright yellow needles decomposing at about 250°:

0·1619 gave 0·4277 CO_2 and 0·0629 H_2O. C = 72·6; H = 4·3.

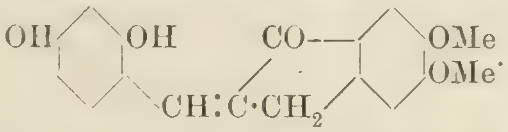
$C_{17}H_{12}O_4$ requires C = 72·9; H = 4·3 per cent.

The *acetyl* derivative was prepared by digesting with acetic anhydride and sodium acetate for half an hour; the product was decomposed by water, and the precipitate collected and crystallised from alcohol, from which it separated readily in pale yellow needles melting at 199°:

0·1486 gave 0·3850 CO_2 and 0·0580 H_2O. C = 70·7; H = 4·3.

$C_{19}H_{14}O_5$ requires C = 70·8; H = 4·3 per cent.

2′ : 4′-*Dihydroxy*-5 : 6-*dimethoxy*-2-*benzylidene*-1-*hydrindone*,



This important substance is produced by the condensation of β-resorcylaldehyde and 5 : 6-dimethoxy-1-hydrindone in the presence of hydrogen chloride (compare p. 1093). β-Resorcylaldehyde (3 grams) and dimethoxyhydrindone (4 grams) are dissolved in glacial acetic acid (20 c.c.) and gradually saturated with hydrogen chloride, the whole being well cooled during the operation. The colourless solution rapidly becomes yellow, then brown, and finally red, and a red crystalline precipitate separates. After one hour the whole is filtered by the aid of the pump, and the dark red solid, which is a mixture of the hydrochlorides of the unsaturated ketone and of a pyranol base,* is treated with sodium acetate when a brownish-red colour changes to yellowish-brown. The precipitate is collected and washed with acetic acid, which removes the pyranol base, and leaves a light brown, crystalline solid which is purified by crystallisation from a large quantity of alcohol. It crystallises in flakes and decomposes at about 240° :

0·1284 gave 0·2928 CO_2 and 0·0672 H_2O. C = 62·2 ; H = 5·8.
$C_{18}H_{16}O_5,2H_2O$ requires C = 62·1 ; H = 5·7 per cent.

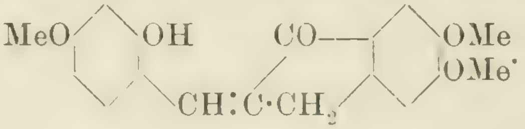
It appears therefore that this substance contains 2 mols. of water of crystallisation, but the direct determination of the latter yielded only approximate results, owing to the fact that it is not removed readily until about 150°, at which temperature the substance slowly decomposes :

0·2565 lost 0·0315 at 150°. H_2O = 12·3.
$C_{18}H_{16}O_5,2H_2O$ contains H_2O = 10·4 per cent.

The *diacetyl* derivative is obtained when the hydrindone is digested with acetic anhydride and sodium acetate in the usual manner, and separates from alcohol in colourless needles which melt at 193° :

0·1771 gave 0·4335 CO_2 and 0·0844 H_2O. C = 66·7 ; H = 5·3.
$C_{22}H_{20}O_7$ requires C = 66·7 ; H = 5·0 per cent.

2'-Hydroxy-4' : 5 : 6-trimethoxy-2-benzylidene-1-hydrindone,



This interesting substance, which is so closely allied to trimethylbrazilin, is readily obtained in the following manner :

p-Methoxysalicylaldehyde (5 grams) and 5 : 6-dimethoxy-1-hydrindone (5 grams) are dissolved in methyl alcohol, a solution of caustic potash (4 grams) in methyl alcohol is then added, and the product boiled for half an hour, cooled, and the red solution acidified with acetic acid. The yellow precipitate is collected, washed with alcohol, in which it is almost insoluble, and crystallised from boiling *iso*amyl alcohol, from which it separates in pale yellow prisms which gradually decompose at 240°, but do not melt when plunged into a bath heated at 280°. After drying at 100° the following results were obtained on analysis :

0·1620 gave 0·4110 CO_2 and 0·0802 H_2O. C = 69·2 ; H = 5·5.
$C_{19}H_{18}O_5$ requires C = 69·6 ; H = 5·5 per cent.

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* This and other similar bases will form the subject of a future communication.

The *potassium* derivative crystallises from dilute alcohol in glistening, orange-yellow needles which resemble lead iodide :

0·4106 gave 0·0972 K_2SO_4. K = 10·6.

$C_{19}H_{17}O_5K$ requires K = 10·7 per cent.

The *hydrochloride* is obtained in deep crimson needles when the solution of the ketone in acetic acid is saturated with hydrogen chloride. It was collected by the aid of the pump, drained on porous porcelain, and exposed to the air until dry :

0·2981 gave 0·1096 AgCl. Cl = 9·0.

$C_{19}H_{18}O_5,HCl$ requires Cl = 9·7 per cent.

In contact with much water, this hydrochloride is only very gradually dissociated into its constituents.

The *acetyl* derivative was prepared in the usual manner by digesting the substance with acetic anhydride and sodium acetate for ten minutes and pouring the product into water. It separates from alcohol, in which it is sparingly soluble, in pale yellow needles or prisms and melts at 175° :

0·1729 gave 0·4337 CO_2 and 0·0862 H_2O. C = 68·4 ; H = 5·5.

$C_{21}H_{20}O_6$ requires C = 68·5 ; H = 5·4 per cent.

The *dibromide* of the *acetyl* derivative. The solution of the acetyl derivative in chloroform readily absorbs bromine with the formation of a peculiar red dibromide. The acetyl derivative (5 grams) dissolved in chloroform (100 grams) was mixed with bromine (2·2 grams) when, after a short time, a deep red precipitate separated which was collected by the aid of the pump and dried in a desiccator ; it yielded only approximate results on analysis :

0·1805 gave 0·1479 AgBr. Br = 34·8.

$C_{21}H_{20}O_6Br_2$ requires Br = 30·3 per cent.

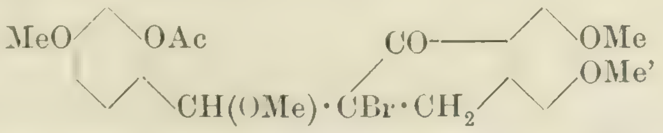
Boiling methyl alcohol converted this red dibromide into a bright yellow substance, which under the microscope was seen to consist of needles. It decomposes at about 270° and dissolves somewhat in boiling alcohol or acetic acid, but is very sparingly soluble in other solvents :

0·1230 gave 0·2510 CO_2 and 0·530 H_2O. C = 54·8 ; H = 4·7.

0·1493 ,, 0·0568 AgBr. Br = 16·2.

$C_{22}H_{23}O_7Br$ requires C = 55·1 ; H = 4·9 ; Br = 16·7 per cent.

This interesting *bromomethoxy*-compound, the constitution of which is evidently represented by the formula

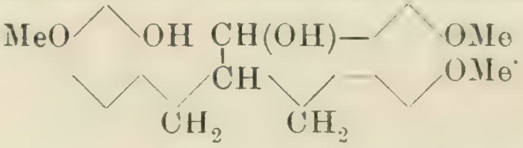


or the analogous formula containing the grouping, ·CHBr·C(OMe)<, will be further investigated. Somewhat similar substances to the above have been obtained by A. Werner (*Ber.*, 1906, **39**, 35) who showed that anisylideneacetophenone dibromide,

$$MeO{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}C_6H_5,$$

when digested with methyl alcohol is converted into the compound $MeO{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CHBr{\cdot}CO{\cdot}C_6H_5$.

1 : 2′-*Dihydroxy*-4′ : 5 : 6-*trimethoxy*-2-*benzylhydrindene*,



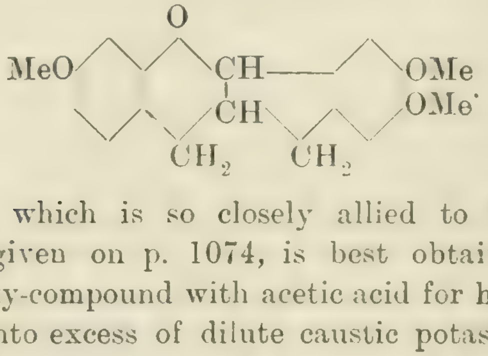
This interesting substance, from which the formula given on p. 1074 of the introduction is derived by the simple substitution of hydrogen of the benzyl group by hydroxyl, is not easy to obtain, but it was ultimately prepared in the following manner. The pure potassium derivative of 2′-hydroxy-4′ : 5 : 6-trimethoxy-2-benzylidenehydrindone is dissolved in hot water and the red solution heated in a flat basin on the water-bath with a large excess of sodium amalgam (compare footnote, p. 1089), care being taken, by the frequent addition of acetic acid, that the solution is always only slightly alkaline. When the solution has become colourless, the product is filtered, acidified with acetic acid, and the colourless precipitate collected by the aid of the pump, dried on porous porcelain and purified by precipitating its benzene solution with light petroleum :

0·1170 gave 0·2948 CO_2 and 0·0706 H_2O. C = 68·7 ; H = 6·7.

$C_{19}H_{22}O_5$ requires C = 69·1 ; H = 6·7 per cent.

When freshly prepared this substance is completely soluble in cold potash but, when digested with solvents, it gradually becomes insoluble owing to its conversion into

4′: 5 : 6-*Trimethoxy*-1 : 2-*hydrindochroman*,



This substance, which is so closely allied to the formula for trimethylbrazilin given on p. 1074, is best obtained by digesting the above dihydroxy-compound with acetic acid for half an hour. The product is poured into excess of dilute caustic potash, the precipitate collected, dissolved in chloroform and precipitated by light petroleum ; it is then further purified by careful precipitation from its alcoholic solution by water, when it separates in flocks, which under the microscope are seen to consist of minute needles :

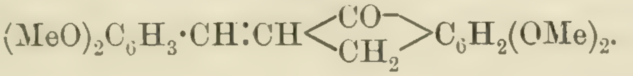
0·1140 gave 0·3024 CO_2 and 0·0670 H_2O. C = 72·3 ; H = 6·5.

$C_{19}H_{20}O_4$ requires C = 73·1 ; H = 6·4 per cent.

This chroman is readily soluble in alcohol, ether, benzene, or chloroform, but is almost insoluble in light petroleum in the cold.

During the course of one preparation a substance was obtained which separated from alcohol in glistening plates, melted at 115°, and dissolved in sulphuric acid yielding a red solution, which became blue on the addition of water. The quantity obtained was unfortunately so small that we were unable to investigate it further.

2′ : 4′ : 5 : 6-*Tetramethoxy*-2-*benzylidene*-1-*hydrindone*,



$$(\mathrm{MeO})_2\mathrm{C_6H_3{\cdot}CH{:}CH}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CH_2}\end{smallmatrix}>\mathrm{C_6H_2(OMe)_2}.$$

This substance has been obtained in two different ways :

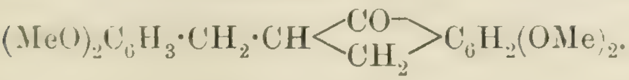
I. *By the Methylation of the corresponding* 2′ : 4′-*Dihydroxy-compound.*—The dihydroxy-compound (p. 1097) dissolves in excess of caustic potash with a red colour, and, when the solution is shaken with methyl sulphate, this soon changes to yellow and, on acidifying, deposits a yellow precipitate which consists, apparently, of the trimethoxy-compound (p. 1098). If, however, the action of the methyl sulphate and caustic potash is continued, the tetramethoxy-compound separates as a yellow solid which is collected and, after recrystallisation, melts at 189°.

II. *By the Condensation of Dimethyl-β-resorcylaldehyde* with 5 : 6-*Dimethoxy*-1-*hydrindone.*—Equal weights of these substances (5 grams) are dissolved in alcohol (50 c.c.), mixed with two or three drops of warm, concentrated aqueous potash, when the condensation product separates immediately. The precipitate is collected by the aid of the pump and purified by recrystallisation from hot alcohol, from which it is obtained in small yellow prisms melting at 189° :

0·1480 gave 0 3818 CO_2 and 0·0790 H_2O. C = 70·4 ; H = 5·9.

$C_{20}H_{20}O_5$ requires C = 70·6 ; H = 5·9 per cent.

2′ : 4′ : 5 : 6-*Tetramethoxy*-2-*benzyl*-1-*hydrindone*,



$$(\mathrm{MeO})_2\mathrm{C_6H_3{\cdot}CH_2{\cdot}CH}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CH_2}\end{smallmatrix}>\mathrm{C_6H_2(OMe)_2}.$$

This substance is obtained when the above tetramethoxybenzylidene-hydrindone is digested, in alcoholic solution, with sodium amalgam for half an hour and is precipitated, on the addition of water, in colourless flocks. It was purified by dissolving in benzene and precipitating with light petroleum:

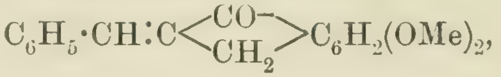
0·1322 gave 0·3408 CO_2 and 0·0810 H_2O. C = 70·3; H = 6·8.
$C_{20}H_{22}O_5$ requires C = 70·2; H = 6·4 per cent.

This compound, which appears to be also formed when the benzylidenehydrindone is reduced by zinc and acetic acid, dissolves in concentrated sulphuric acid with an intense purple colour which becomes blue on dilution with water. It yields a crystalline oxime which was, however, not analysed or further investigated.

Other Derivatives of 5 : 6-*Dimethoxy*-1-*hydrindone.*

In addition to the substances already described, the following derivatives of 5 : 6-dimethoxy-1-hydrindone have also been prepared, in each case by adding a few drops of concentrated, aqueous potash to a warm, alcoholic solution of equimolecular quantities of the hydrindone and the corresponding aldehyde.

5 : 6-*Dimethoxy*-2-*benzylidene*-1-*hydrindone*,

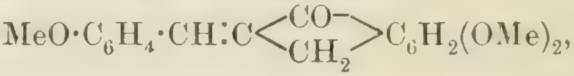


$$C_6H_5\cdot CH\!:\!C{<}\begin{matrix}CO-\\CH_2\end{matrix}{>}C_6H_2(OMe)_2,$$

melts at 174°:

0·1216 gave 0·3421 CO_2 and 0·0647 H_2O. C = 76·7; H = 5·9.
$C_{18}H_{16}O_3$ requires C = 77·1; H = 5·7 per cent.

5 : 6-*Dimethoxy*-2-*anisylidene*-1-*hydrindone*,



$$MeO\cdot C_6H_4\cdot CH\!:\!C{<}\begin{matrix}CO-\\CH_2\end{matrix}{>}C_6H_2(OMe)_2,$$

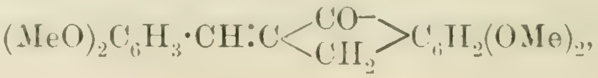
melts at 188°:

0·1295 gave 0·3489 CO_2 and 0·0671 H_2O. C = 73·5; H = 5·8.
$C_{19}H_{18}O_4$ requires C = 73·6; H = 5·8 per cent.

The *hydrochloride* separates in orange-red flocks, which, under the microscope, are seen to consist of needles, when the solution of the ketone in glacial acetic acid is saturated with hydrogen chloride:

0·1662 gave 0·0673 AgCl. Cl = 9·9.
$C_{19}H_{18}O_4,HCl$ requires Cl = 10·1 per cent.

5 : 6-*Dimethoxy*-2-*veratrylidene*-1-*hydrindone*,

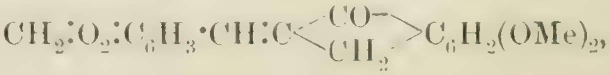


$$(MeO)_2C_6H_3\cdot CH\!:\!C{<}\begin{matrix}CO-\\CH_2\end{matrix}{>}C_6H_2(OMe)_2,$$

melts at 193°:

0·2111 gave 0·5451 CO_2 and 0·1136 H_2O. C = 70·4; H = 6·0.
$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

5 : 6-*Dimethoxy*-2-*piperonylidene*-1-*hydrindone*,



$$CH_2\!:\!O_2\!:\!C_6H_3\cdot CH\!:\!C{<}\begin{matrix}CO-\\CH_2\end{matrix}{>}C_6H_2(OMe)_2,$$

melts at 245°.

0·1637 gave 0·4217 CO_2 and 0·0765 H_2O. C = 70·3 ; H = 5·2.

$C_{19}H_{16}O_5$ requires C = 70·4 ; H = 4·9 per cent.

Of these four compounds, the piperonylidene derivative separates immediately the constituents are mixed, the veratrylidene derivative separates in about one minute, and the others in about two minutes.

They all crystallise from alcohol or, better, from acetic acid in pale yellow needles or prisms, the benzylidene derivative being the most and the piperonylidene derivative the least soluble.

Benzaldehyde is frequently used as a reagent for cyclic and other ketones containing the grouping, $\cdot CO \cdot CH_2 \cdot$, but piperonal will probably be found to be much more serviceable for this purpose on account of the sparing solubilities and high melting points which usually characterise condensation products obtained with the aid of this aldehyde.

The authors wish to state that much of the expense entailed during this research has been met by grants from the Government Grant Committee of the Royal Society and from the Research Fund of the Chemical Society.

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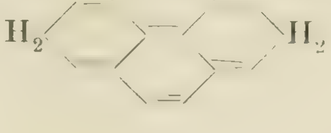
CIII.—*The Action of Aluminium Chloride on Naphthalene.*

By ANNIE HOMER, B.A., Bathurst Student of Newnham College, Cambridge.

Preparation and Identification of ββ-Dinaphthyl.

DURING the course of a series of investigations on nickel carbonyl, Dewar and Jones (Trans., 1904, **85**, 212) observed that nickel carbonyl and naphthalene in presence of aluminium chloride gave a small yield of a hydrocarbon of which the melting point, solubility, and analyses corresponded with those of a compound prepared by Bischoff (*Ber.*, 1890, **23**, 1905) by the action of methyl chloride on a mixture of naphthalene and aluminium chloride. Bischoff had proposed for this hydrocarbon the formula $C_{16}H_{12}$ and had represented it as :



Dewar and Jones further stated that nickel carbonyl acting on benzene and aluminium bromide gave some of the above compound, whilst with benzene and aluminium chloride the products were benzaldehyde and anthracene with no trace of Bischoff's hydrocarbon.

As it seemed of some interest to investigate the above apparent difference in the specific influence of the two aluminium salts on the products of the reaction, it was with this object primarily that, at the suggestion of Mr. H. O. Jones, the work about to be described was undertaken.

The first point requiring explanation was whether the substitution of aluminium bromide for aluminium chloride in a Friedel and Crafts' reaction always leads to a difference in the products of the reaction, and if not, whether, as in the above case, it does so only when acting conjointly with nickel carbonyl. It seemed as if an explanation of all the different methods of formation of the hydrocarbon $C_{16}H_{12}$ should incidentally also furnish the answer to the above question, an anticipation that has been realised.

I. *The Action of Nickel Carbonyl on Benzene in the presence of Aluminium Bromide.*

Six experiments were carried out under the conditions given in the paper by Dewar and Jones. The aluminium bromide used was freshly prepared, (i) by treating aluminium powder with bromine and distilling off the aluminium bromide and (ii) by passing bromine over red-hot aluminium turnings. The result in each case was the production of benzaldehyde and anthracene without a trace of the hydrocarbon $C_{16}H_{12}$. It may therefore be taken as established that this hydrocarbon cannot be formed from benzene. Moreover, in a simple Friedel and Crafts' reaction, namely the formation of benzophenone, aluminium bromide was used instead of aluminium chloride without in any way affecting the final products of the reaction.

II. *The Action of Nickel Carbonyl on Naphthalene in presence of Aluminium Chloride* (referred to subsequently as Dewar and Jones' reaction).

The yield of the hydrocarbon was never more than 2 per cent. of the naphthalene taken, and whether the reaction took place in the cold or at 100° there was always formed a considerable amount of a tarry product.

III. *The Action of Methyl Chloride on Naphthalene in presence of Aluminium Chloride* (referred to subsequently as Bischoff's reaction).

The crystalline hydrocarbon prepared by this method melted at 181°, and its previously assumed identity with Dewar and Jones' hydrocarbon (m. p. 181°) was definitely proved by the fact that a mixture of the two melted at the same temperature.

Neither Dewar and Jones nor Bischoff had extended their investigations to the tarry residues left after the isolation of the crystalline hydrocarbon; the series of new substances obtained from the two tars and about to be described in this paper was found to be the same, thereby furnishing additional proof of the identity of the effects produced on naphthalene in each of the reactions II and III.

IV. *The Action of Aluminium Chloride alone on Naphthalene.*

During the course of the work connected with the testing of methods II and III it had been noticed that aluminium chloride and naphthalene, when mixed in equimolecular proportions and kept in sealed tubes or in flasks connected with calcium chloride tubes, darkened to a deep purple colour and that after four weeks a considerable amount of tar had been formed. Moreover, on heating such mixtures at 100° for periods varying from thirty minutes to six hours the tar was formed rapidly and yielded, not only a crystalline hydrocarbon melting at 181°, but also a further series of products in every way the same as those obtained in II and III.

Mixtures of this hydrocarbon with either Dewar and Jones' or with Bischoff's hydrocarbon did not affect the melting point of these, thus proving the identity of the three substances.

Hence it has been established that neither nickel carbonyl nor methyl chloride is essential to the reaction occurring between aluminium chloride and naphthalene, although the presence of nickel carbonyl has, at the ordinary temperature, an accelerating effect.

Friedel and Crafts (*Compt. rend.*, 1885, **100**, 692) studied the action of aluminium chloride (1 part) on naphthalene (4 parts) and noticed that these two substances reacting at temperatures between 100° and 160° gave $\beta\beta$-dinaphthyl, $C_{20}H_{14}$, melting at 187°, and a mixture of hydrodinaphthylenes. This value for the melting point of $\beta\beta$-dinaphthyl was corroborated by Watson Smith. Friedel and Crafts found that $\beta\beta$-dinaphthyl was not affected by heating with a further quantity of aluminium chloride, whereas the hydrodinaphthylenes were converted to hydronaphthalenes (b. p. = 210° circ./760 mm.). They apparently did not investigate the products of higher boiling point.

It therefore became necessary to ascertain whether the formula for the hydrocarbon is $C_{16}H_{12}$ as proposed by Bischoff and accepted by Dewar and Jones, or $C_{20}H_{14}$ as given by Friedel and Crafts.

Dewar and Jones found C = 93·7 and 93·9; H = 5·63 and 5·76.

$C_{16}H_{12}$ requires C = 94·12; H = 5·88.
$C_{20}H_{14}$ „ C = 94·49; H = 5·51 per cent.

It is obvious that for a compound containing so high a percentage of carbon, analysis alone furnishes insufficient evidence. Bischoff made no molecular weight determination, and the results obtained by Dewar and Jones varied considerably owing to the experimental difficulties due to the high boiling point and slight solubility of the substance.

Dewar and Jones found M.W. values varying between 180 and 263.

$C_{20}H_{14}$ requires M.W. = 254.
$C_{16}H_{12}$ „ M.W. = 204.

Study of the picrate supplied the data for the necessary decision. Bischoff had prepared a picrate of his hydrocarbon, and found its melting point to be 181°, whilst according to Watson Smith (Trans., 1885, 47, 104) the picrate of $\beta\beta$-dinaphthyl melts at 183°. The picrates of the hydrocarbons prepared in the course of the present investigation according to methods II, III, and IV were in each case found to melt at 183°, and the analyses of these picrates (see experimental part) gave the formula $C_{20}H_{14},2[C_6H_2(NO_2)_3\cdot OH]$. Therefore the hydrocarbon under investigation must be taken not to have the formula $C_{16}H_{12}$, but $C_{20}H_{14}$, that of $\beta\beta$-dinaphthyl. It must, however, be pointed out that all attempts to reconcile the value found for the melting point with 187°, that given by Friedel and Crafts, were unsuccessful; in spite of repeated recrystallisation from benzene and ethylene dibromide, the melting point remained constant at 181° (uncorr.).

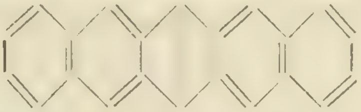
The formation of the hydrocarbon thus recognised as $C_{20}H_{14}$, from naphthalene and aluminium chloride, which has been shown to be independent of the presence of either nickel carbonyl or methyl chloride, is therefore one of simple condensation.

Preparation and Investigation of Other Products formed in the Reaction between Naphthalene and Aluminium Chloride.

These products were studied in some detail and were neither hydrodinaphthylenes nor hydronaphthalenes, as had been obtained by Friedel and Crafts. The following substances were isolated:

(i) *From the fraction boiling at* 215—225°/10*mm*., *a pale yellow oil.* Analysis and molecular weight determinations gave for this substance the formula $C_{14}H_{16}$. The attempts to elucidate its constitution did not lead to conclusive results, although they afforded certain indications. The formation of a naphthalenecarboxylic acid points to a homologue of naphthalene. Moreover, it is known that the action of aluminium chloride on benzene results in the production of alkylbenzenes and diphenyl, whilst with homologues of benzene the monoalkyl derivatives interact, yielding di- or tri-derivatives; hence it would seem justifiable to infer that the new substance $C_{14}H_{16}$, derived from naphthalene under conditions comparable to the above, is tetramethyl- or diethyl-naphthalene, more probably the former.

(ii) *From the fraction boiling above* 300°/10*mm.*, *a red, transparent, resinous, highly fluorescent solid.*—Analyses of this substance and of its nitro- and nitro-oxidation derivatives establish for it the formula $C_{26}H_{22}$ (see p. 1111). It is suggested that it is a homologue of dinaphthanthracene, $C_{22}H_{14}$ (Russig, *J. pr. Chem.*, 1900, [ii], **62**, 30):

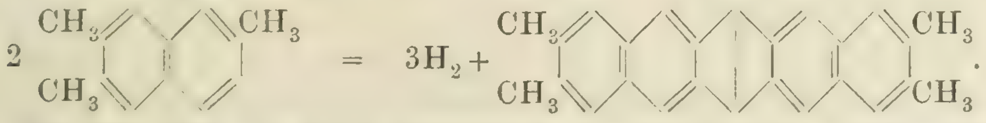


on the following grounds:

(*a*) The intense fluorescence of the substance suggests the presence of an anthracenoid linking which can be expressed in the above formula, thus leaving C_4H_8 to be accounted for by side chains.

(*b*) The actual presence of at least one alkyl side chain, probably methyl (see p. 1112), is indicated by the composition of the nitro-oxidation product.

(*c*) From the facts known of the action of aluminium chloride on benzene and its homologues already referred to above, it seems justifiable to infer that the condensation occurring here has resulted in the formation of a symmetrical product, namely, tetramethyldinaphthanthracene. During the course of the present investigation on naphthalene it has been demonstrated that besides *ββ*-dinaphthyl (substance B), there is also produced an alkylated naphthalene (substance A); under the influence of the aluminium salt the monoalkylated naphthalenes probably first formed would be converted into di-, tri-, or tetra-alkylnaphthalene; and two molecules of the trimethyl derivative so produced might, in the presence of more aluminium chloride, condense with elimination of hydrogen to form the compound, $C_{26}H_{22}$, thus:



The fact that no alkyl derivatives of naphthalene other than substance A (identified as either diethyl- or tetramethylnaphthalene) have been isolated, and that the yield of A relatively to that of C, the supposed condensation product of the alkylated naphthalene, was always small, may be taken to lend some support to this interpretation of the reaction.

(iii) *From the residue left after vacuum distillation by fractional precipitation, a yellowish red solid.*—This does not distil in a vacuum at the temperature at which Jena glass softens. Analysis and molecular weight determinations of the substance itself and study of four bromo-derivatives would seem to prove conclusively that the formula is $C_{40}H_{26}$. It is probable that the compound is tetranaphthyl and is formed by the condensation of either four naphthalene or two $\beta\beta$-dinaphthyl molecules. The nature of the process has not been elucidated in the course of this investigation.

EXPERIMENTAL.

(1) Intimate mixtures of aluminium chloride (4 mols.) and naphthalene (4 mols.) were treated with nickel carbonyl (1 mol.) and left in sealed tubes for one to six hours at 100°, or were left in flasks connected with calcium chloride tubes at the ordinary temperature for ten to fourteen days (Dewar and Jones' reaction); (2) a slow current of methyl chloride was passed for two to three hours through a mixture of aluminium chloride (19 grams) and naphthalene (95 grams) kept between 80° and 90° (Bischoff's reaction); (3) mixtures of aluminium chloride (1 mol.) and naphthalene (1 mol.) in flasks connected with calcium chloride tubes were kept for one to three hours at 100°.

In each case the tarry residue was treated with water and hydrochloric acid, after which it was either allowed to cool and then separated by filtration into its solid and liquid constituents, or treated, while still hot, with benzene, and the extract so obtained dried over calcium chloride and distilled. The solid obtained by either method was then examined; after the rejection of the portions boiling below 260°/760 mm. and of any unchanged naphthalene, it was subjected to fractional distillation and subsequent fractional precipitation, when the following products were collected:

A. 215—225°/10 mm. Pale yellow oil, soluble in light petroleum and xylene.

B. 250—300°/10 mm. Viscid, deep yellow oil, solidifying to crystals melting at 181°, which in the cold are almost insoluble in light petroleum and xylene.

C. Above 300°/10 mm. Red, viscous oil, which on cooling sets to a brittle, resinous solid, becoming plastic at 49—50°, and is soluble in light petroleum and xylene.

D. A yellowish-red powder, soluble in xylene and insoluble in light petroleum, which is obtained from the residue left after the vacuum distillation by extracting with hot xylene and then precipitating with light petroleum. The repetition of this process yielded the solid in a pure condition.

The difference in solubility of the four substances *A*—*D* in xylene and light petroleum made it possible to devise other processes of separation of *B* from *A* and *C*, and of *C* from *D*; these processes, the details of which need not be given here, did not involve complete fractional distillation, and thus obviated the difficulty due to the tendency of the higher boiling constituents of the tar to decompose explosively.

The approximate percentage yield in terms of the original naphthalene was:

A.	1	impure
B.	2—3	,,
C.	10—15	,,
D.	10—12	,,

Increase in the time allowed for the action of aluminium chloride on naphthalene, or rise in the temperature at which the reaction was conducted, caused a decrease in the amount of residual unchanged naphthalene, and an increase in the amount of *C* and *D* produced relatively to *A* and *B*.

Substance A.—This is a pale yellow oil with a very disagreeable odour, extremely soluble in ethylene dibromide, benzene, xylene, toluene, alcohol, light petroleum, ether, glacial acetic acid, or carbon disulphide. The pure oil, as obtained after many fractionations, could be kept for some three or four weeks without appreciable alteration in colour, but unless thus purified it darkened even in diffused light and became markedly fluorescent. Solutions, even of the pure substance, which were slightly fluorescent at first, soon darkened, and the fluorescence became intensely blue. The oil and its solutions showed no absorption band in the visible portion of the spectrum.

The mean values of six analyses varying from $C = 90{\cdot}3$ to $91{\cdot}6$, and $H = 7{\cdot}74$ to $8{\cdot}52$, and of five molecular weight determinations varying from 176 to 195 were:

$$C = 90{\cdot}9 ;\ H = 8{\cdot}09 ;\ \text{M.W.} = 186.$$

$$C_{14}H_{16} \text{ requires } C = 91{\cdot}2 ;\ H = 8{\cdot}8 \text{ per cent.} ;\ \text{M.W.} = 184.$$

There were indications of the formation of a picrate, of a bromine substitution derivative, and of an oxidation product due to the action of alkaline permanganate, but none of these derivatives could be isolated. The action of 10 per cent. nitric acid yielded an oxidation product, which was a crystalline acid free from nitrogen, melting with decomposition at 204—208°, giving the fluorescein test, and evolving naphthalene when heated with sodium. It may therefore be inferred that this oxidation product is a naphthalenecarboxylic acid. The very small amount of this substance available (less than 0·1 gram) was, through the silver salt, converted into the methyl ester, which, after ten crystallisations from ether, was obtained in white needles with the constant melting point 119—120°, but could not be further investigated.

Substance B.—The yellow crystals purified by several recrystallisations from benzene, melted at 181° and possessed the properties fully described by Dewar and Jones. A spectroscopic examination of solutions showed absence of absorption bands in the visible portion of the spectrum. As already stated (p. 1106), the new work on this substance supplied evidence for assigning to it the formula $C_{20}H_{14}$ and identifying it with Friedel and Crafts' ββ-dinaphthyl.

The picrate was obtained by treating a benzene solution of 2·5 grams of the purified hydrocarbon with a benzene solution of 2·3 grams of picric acid, and recrystallising the resulting product from benzene until the melting point became constant at 183°.

0·26525 gave 0·5180 CO_2 and 0·0680 H_2O. C = 53·3; H = 2·87.
0·2240 „ 23·4 c c. moist nitrogen at 17·5° and 761 m.m. N = 12·18.
$C_{16}H_{12},2[C_6H_2(NO_2)_3\cdot OH]$ requires C = 50·05; H = 2·72; N = 12·7 per cent.
$C_{20}H_{14},2[C_6H_2(NO_2)_3\cdot OH]$ requires C = 53·93; H = 2·79; N = 11·8 per cent.

From these analyses it is clear that the formula for the picrate must be $C_{20}H_{14},2[C_6H_2(NO_2)_3\cdot OH]$; hence the formula for the parent hydrocarbon is $C_{20}H_{14}$, and not $C_{16}H_{12}$, as had been previously assumed.

Some additional evidence for the $C_{20}H_{14}$ formula was obtained by the study of its quinones. By varying the proportions of the chromium trioxide used (1 mol. of $C_{20}H_{14}$ either to 8 or to 4 of CrO_3), two quinones differing in solubility and melting point were obtained. The one melting and decomposing at 250°, which is insoluble in alcohol but can be recrystallised from glacial acetic acid, exhibited the properties of the quinone described by Watson Smith (*loc. cit.*) and Chattaway (Trans., 1895, 67, 662), and gave on analysis numbers agreeing with the ββ-di-α-naphthaquinone formula $C_{20}H_{10}O_4$ which they assigned to it. The other quinone, which melts and decomposes at 161—167°, is very soluble in glacial acetic acid, but can be recrystallised from alcohol; it gave on analysis results in fair agreement with the formula $C_{20}H_{12}O_2$ for β-naphthylnaphthaquinone (Chattaway, *loc. cit.*).

Substance C is a red, transparent solid with a green fluorescence. It is very soluble in benzene, toluene, xylene, light petroleum, ether, carbon disulphide, carbon tetrachloride, glacial acetic acid, ethylene dibromide, and to a less extent in alcohol. Its solutions show strong fluorescence of tints dependent on the concentration. This property is so marked that solutions containing one part of the solute in one million of the solvent still exhibit fluorescence. The spectroscopic examination of this hydrocarbon, both in the visible and ultraviolet portions of the spectrum, yields results of considerable interest, which are still being investigated, and which will be dealt with in a subsequent paper. These results will be compared with those which may be obtained from a similar examination of dinaphthanthracene and of the hydrocarbons described in this paper. It is, however, pertinent to the present investigation to mention that dilute solutions show two characteristic absorption bands, the one in the blue, the other in the violet region. The following numbers were obtained on analysis:

0·2354 gave 0·8105 CO_2 and 0·1245 H_2O. C = 93·9; H = 5·92.
0·1570 ,, 0·5395 CO_2 ,, 0·0825 H_2O. C = 93·71; H = 5·88.
M.W. by cryoscopic method in (I) benzene, 344 and 317; (II) ethylene dibromide, 318.
$C_{26}H_{22}$ requires C = 93·65; H = 6·35 per cent. M.W. = 334.

There were indications of the formation of a picrate and of sulphonic acids, but in neither case could the product be isolated in a form suitable for analysis. Hydriodic acid was without effect. Whilst alkaline potassium permanganate produced no oxidation, chromium trioxide did so, but in this case also the yield was too small to allow of further investigation. Slightly better success attended the attempt to obtain bromine derivatives; a substitution product was isolated and analysed, but with results which showed that the substance so obtained was not quite pure. The action of fuming nitric acid (five to six parts to one of hydrocarbon), continued at the ordinary temperature for six days, resulted in the formation of a bright yellow nitro-compound, which was purified by precipitation from its chloroform solution by means of light petroleum. This nitro-compound melted at 167°.

0·1203 gave 0·2328 CO_2 and 0·0310 H_2O. C = 52·8; H = 2·75.
0·1000 ,, 11·34 c.c. moist nitrogen at 16·3° and 755·5 mm. N = 13·2.
$C_{26}H_{16}(NO_2)_6$ requires C = 51·7; H = 2·65; N = 13·9 per cent.

The action of ordinary hot concentrated nitric acid yielded an oxidation product, less soluble in chloroform than the above, but sufficiently so to admit of its being purified in the same manner. The substance contained nitrogen; its solubility in sodium carbonate solution characterised it as an acid formed by the substitution of one or more carboxyl for alkyl groups, methyl, ethyl, &c.

0·1641 gave 0·3210 CO_2 and 0·0395 H_2O. C = 53·35; H = 2·69.
0·1774 ,, 16·89 c.c. moist nitrogen at 14° and 761·2 mm. N = 11·29.
$C_{25}H_{14}(NO_2)_5{\cdot}CO_2H$ requires C = 53·0; H = 2·54; N = 11·9 per cent.
$C_{24}H_{12}(NO_2)_5{\cdot}CO_2H$,, C = 52·2; H = 2·26; N = 12·2 ,,

The results obtained are therefore in fair agreement with the assumption that the above nitro-oxidation product had been formed by the introduction into the parent hydrocarbon $C_{26}H_{22}$ of five nitro-groups simultaneously with the substitution of one carboxyl for one methyl rather than for one ethyl group.

Substance D is a very light powder, reddish yellow in colour, insoluble in alcohol, glacial acetic acid, ether, or light petroleum, and very soluble in benzene, toluene, xylene, ethylene dibromide, carbon tetrachloride, carbon disulphide or chloroform. A spectroscopic examination of the substance showed that strong solutions exhibit general absorption, but even in the case of dilute solutions there was no evidence of absorption bands in the visible region of the spectrum. It has not been obtained in a crystalline condition, as it tends to separate from its solutions as a tarry mass unless prepared as described in the earlier part of this paper. The melting point of the amorphous powder cannot be readily taken, as it darkens at about 190—200° and at higher temperatures melts to a tar. Although it could not be obtained crystalline, it was considered as a definite, pure substance, since fractional precipitation had been continued until analyses of samples prepared at different times indicated constancy of composition.

0·1363 gave 0·4728 CO_2 and 0·0660 H_2O. C = 94·7 ; H = 5·41.
0·1978 ,, 0·6826 CO_2 and 0·0948 H_2O. C = 94·1 ; H = 5·37.
0·2348 ,, 0·8190 CO_2 and 0·1159 H_2O. C = 95·0 ; H = 5·53.

M.W. by cryoscopic method in (I) benzene, 524, (II) ethylene dibromide 473 and 517.

$C_{40}H_{26}$ requires C = 94·8 ; H = 5·19 per cent. M.W. = 506.

There were indications of the formation of a picrate, of sulphonic acids and of a nitro-derivative, but in no case were the products suitable for further investigation. Alkaline permanganate, chromium trioxide and ten per cent. nitric acid were without action on the substance.

Further evidence as to the formula for the hydrocarbon was, however, furnished by the analysis of a series of four bromo-substitution products formed by the action of the calculated quantities of bromine on the hydrocarbon in carbon tetrachloride solution. The resulting products were too soluble in benzene, xylene, toluene or carbon tetrachloride to be purified by crystallisation. An attempt was therefore made to obtain them pure by fractional precipitation from their benzene solutions by the addition of alcohol, in which they are almost insoluble. The process was repeated several times, but complete separation from the higher or lower bromo-derivatives was not effected. Hence the analyses do not show perfect agreement with the theoretical numbers; the discrepancies however are not so great but that the results may be taken to support the formula $C_{40}H_{26}$ for the parent hydrocarbon.

(I) 1 *Molecule of* $C_{40}H_{26}$: 2 *Molecules of Bromine.*

0·1961 gave 0·5091 CO_2 and 0·0700 H_2O. C = 70·7 ; H = 4·00.
0·2198 ,, 0·1280 AgBr. Br = 24·8.
$C_{40}H_{24}Br_2$ requires C = 72·3 ; H = 3·6 ; Br = 24·1 per cent.

(II) 1 *Molecule of* $C_{40}H_{26}$: 3 *Molecules of Bromine.*

0·1918 gave 0·4515 CO_2 and 0·0570 H_2O. C = 64·2 ; H = 3·33.
0·2170 ,, 0·1704 AgBr. Br = 33·4.
0·1157 ,, 0·0877 AgBr. Br = 32·2.
$C_{40}H_{23}Br_3$ requires C = 64·6 ; H = 3·1 ; Br = 32·3 per cent.

(III) 1 *Molecule of* $C_{40}H_{26}$: 4 *Molecules of Bromine.*

0·2023 gave 0·4368 CO_2 and 0·0647 H_2O. C = 58·88 ; H = 3·3.
0·2010 ,, 0·1853 AgBr. Br = 39·2.
$C_{40}H_{22}Br_4$ requires C = 58·4 ; H = 2·7 ; Br = 38·9 per cent.

(IV) 1 *Molecule of* $C_{40}H_{26}$: 5 *Molecules of Bromine.*

0·2808 gave 0·5313 CO_2 and 0·0665 H_2O. C = 51·7 ; H = 2·65.
0·2657 ,, 0·2779 AgBr. Br = 44·6.
0·2870 ,, 0·3061 AgBr. Br = 45·4.
$C_{40}H_{21}Br_5$ requires C = 53·3 ; H = 2·3 ; Br = 44·4 per cent.

Summary :

(I) The hydrocarbon to which Bischoff had assigned the formula $C_{16}H_{12}$ cannot be obtained from benzene. Its formation in Dewar and Jones' and Bischoff's reactions respectively does not depend on the presence of either nickel carbonyl or methyl chloride, but is merely due to the condensing effect of aluminium chloride on naphthalene.

(II) This hydrocarbon has not the formula $C_{16}H_{12}$, but is identical with Friedel and Crafts' ββ-dinaphthyl, $C_{20}H_{14}$, formed by a process of simple condensation.

(III) The specific effect of aluminium bromide in the above, as in other Friedel and Crafts' reactions, is the same as that of aluminium chloride.

(IV) From the product of the reaction between aluminium chloride and naphthalene, besides ββ-dinaphthyl, there have also been isolated three new hydrocarbons:

(1) $C_{14}H_{16}$, a homologue of naphthalene, probably tetramethyl- or diethylnaphthalene.

(2) $C_{26}H_{22}$, a substance with interesting spectroscopic properties probably a homologue of dinaphthanthracene $C_{22}H_{14}$.

(3) $C_{40}H_{26}$, which is probably tetranaphthyl formed by a process of condensation.

In conclusion, the author wishes to thank Mr. H. O. Jones, M.A., of Clare College, Cambridge, at whose suggestion this work was begun, for unfailing interest and valuable advice during the progress of this research.

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CIV.—*Molecular Weight of β-Naphthol in Solution in Solid Naphthalene.*

By EDGAR PHILIP PERMAN and JOHN HUGHES DAVIES.

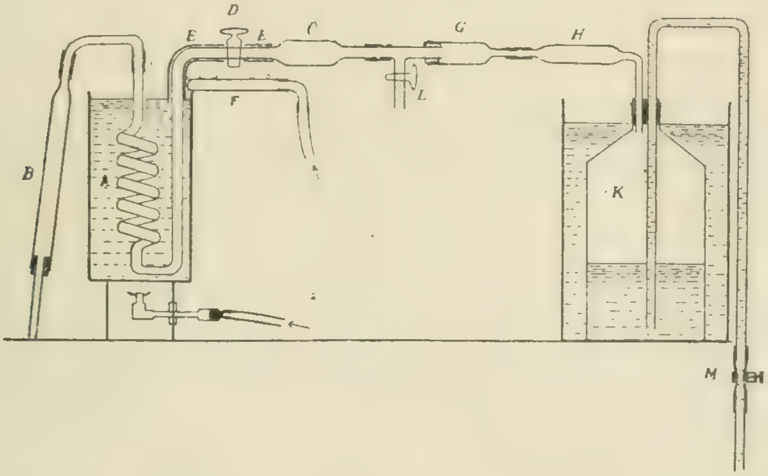
PREVIOUS work on this subject has been carried out by Küster (*Zeitsch. physikal. Chem.*, 1895, **17**, 357) and Speranski (*ibid.*, 1903, **46**, 70); it was thought, however, that their results needed confirmation and extension, and we consequently undertook to measure the vapour pressure of solid naphthalene and of solid solutions of β-naphthol in naphthalene by another method, namely, by passing a current of air over solid naphthalene or the naphthalene solution, and finding by loss of weight the quantity of naphthalene carried off.

Apparatus and Method.—The naphthalene or naphthalene solution was broken into very small fragments and placed in a spiral glass tube *A*, about 1 metre in length (if unwound) and 5 mm. in diameter. The spiral was supported in a thermostat maintained at 70°. This temperature is near the melting point of naphthalene, and was chosen in order to obtain as high a vapour pressure as possible.

The air-current first entered the soda-lime tube *B*, which deprived it of moisture and of carbon dioxide. It then passed into the spiral, where it became saturated with naphthalene vapour; from the spiral it passed through the stopcock *D* into the wide tube *C*, where the main part of the naphthalene condensed. In order to prevent condensation in the tube *EE*, it was heated above the temperature of the bath by a row of small gas-burners, *F*. The glass tube was protected from the flame by two brass tubes, each being split into two lengthwise; the parts were held together by a wire during an experiment.

The air passed from *C* through a calcium chloride tube *G* and a tube *H* containing wet sponge into a large aspirator *K*, which stood in a vessel of water.

The method of conducting an experiment was as follows. The spiral being filled with the solid and in position, air was drawn through it for some hours (this was necessary only for the first experiment with a given sample). The stopcock *D* was then turned off and the condensed naphthalene was removed from *C* by heating it and drawing air through it by means of a capillary tube. The tubes *EE* were removed, and the spiral was taken out of the bath and allowed to cool; it was then disconnected from *B* and the end stoppered. The spiral was cleaned from the oil of the thermostat by immersing it successively in two jars of light petroleum and wiping thoroughly. It was then carefully weighed, replaced in the thermostat, and connected as before. The tubes *EE* were heated, and the stopcock *L* was opened a few moments in order to ensure that the pressure inside *C* was that of the atmosphere before beginning the aspiration. The stopcock *D* was then opened and the aspiration begun, the water being run into a graduated flask.



To bring the experiment to an end, the water stream was stopped by the clip *M*, and the tap *D* turned a few moments later. The spiral was then removed, cleaned, and weighed exactly as before.

The loss of weight gave the weight of naphthalene drawn off by the air-current. The barometric height and the temperature of the aspirator were read at the end of the experiment.

Vapour Pressure of Naphthalene at 70°.—Experiments were made to discover whether the glass spiral lost weight on continued heating in the bath (water covered with oil). It was found that during the first six hours it lost 0·5 milligram, but during the next twelve hours it lost only 0·2 milligram. As the times of heating during the determination of vapour pressure were much less than this, no correction for such loss of weight was made.

To ensure saturation of the air with naphthalene vapour the air was passed through at a very slow rate, and the rate was varied in order to discover whether such variation has any effect on the vapour pressure.

The results are here tabulated:

w = weight of naphthalene drawn off, in grams.
P = barometric height, mm.
V = volume of air at temperature and pressure of aspirator, litres.
p = pressure of air in aspirator (corrected for moisture).
T = temperature of aspirator (absolute).
t = duration of experiment (minutes).

w.	*P.*	*V.*	*p.*	*T.*	*t.*	*V.P.*
0·1461	758·5	5·530	746·2	287·4	300	3·742
0·1466	755·1	5·530	742·5	287·7	240	3·760
0·1462	749·3	5·530	736·6	287·9	310	3·754
0·1456	765·2	5·530	751·9	288·6	422	3·749
				Mean..................		3·751

Here no connexion can be traced between the vapour pressure and the rate of the air-current, so that the air was evidently saturated with the vapour.

A somewhat similar method was used by Allen (Trans., 1900, **77**, 400), who found 3·80 at this temperature (read from his curve). Allen's experiments do not seem entirely satisfactory, as he did not cause the air to be saturated with the vapour, but found the saturation pressure by a method of extrapolation. Speranski, using a differential tensimeter, obtained the value 2·917 at the same temperature, but this we believe to be erroneous.

Vapour Pressure of β-Naphthol.—This was measured in exactly the same way as the vapour pressure of naphthalene. The following results were obtained:

w.	*P.*	*V.*	*p.*	*T.*	*t.*	*V.P.*
0·0050	759·2	5·530	748·0	286·0	305	0·1135
0·0050	758·1	5·530	747·2	285·5	285	0·1133
				Mean		0·1134

The vapour pressure was less than 3 per cent. of that of naphthalene. This would cause only a slight error in the dilute solutions employed. An approximate correction has, however, been introduced by reckoning the vapour pressure of the β-naphthol in the solid solution to bear the same ratio to the vapour pressure of the pure substance as the quantity of β-naphthol present bore to the total mass of the mixture.

Vapour Pressure of Solid Solutions of β-Naphthol in Naphthalene.—The solutions were made by melting together the required proportions of the substances in a sealed tube and allowing to cool. The solid mass was then broken into small fragments and the spiral was filled with them. It was refilled after every two experiments. The following are the results:

C = concentration, parts of β-naphthol to 100 parts of naphthalene.

C.	*w.*	*P.*	*V.*	*p.*	*T.*	*t.*	*V.P.*
5	0·1379	763·9	5·530	748·8	290·6	285	3·585
5	0·1383	761·3	5·530	746·1	290·7	325	3·597
5	0·1385	759·3	5·530	744·5	290·3	265	3·595
10	0·1357	768·4	5·530	755·4	288·2	255	3·489
10	0·1356	766·1	5·530	752·3	289·2	260	3·459
10	0·1334	767·4	5·530	752·9	290·0	310	3·457
10	0·1350	763·7	5·530	749·2	290·0	295	3·500
15	0·1308	770·7	5·530	756·6	289·5	240	3·383
15	0·1306	770·2	5·530	755·8	289·9	285	3·384
15	0·1300	765·9	5·530	751·3	290·1	255	3·372

The vapour pressures of the solutions and the molecular weights calculated from them are here tabulated:

C.	Mean *V.P.*	Mean *V.P.* corrected for *V.P.* of β-naphthol.	*M.W.* (from uncorrected *V.P.*).	*M.W.* (from corrected *V.P.*).
5	3·592	3·587	151·0	146·4
10	3·476	3·466	174·6	168·5
15	3·380	3·365	194·1	186·5

Summary.—Since the normal molecular weight of β-naphthol is 144, it appears from these experiments that in dilute solid solutions β-naphthol has the same molecular weight as in the gaseous state, whilst it associates in more concentrated solutions. These results agree approximately with those of Speranski (*loc. cit.*), who obtained the following numbers:

Number of mols. β-naphthol to 100 mols. mixture	14·6	17·3	17·4	24·6	33·6
M.W.	198	249	245	257	255

They are somewhat in opposition to those of Küster, whose conclusion was that the molecular weights in the crystalline state were 288 and 256 respectively, and that in isomorphous mixtures a compound, $C_{10}H_8,C_{10}H_7\cdot OH$, was formed, but the experiments leading to this result do not seem very convincing.

In calculating the molecular weights, it has to be assumed that the lowering of vapour pressure follows the same laws as in the case of liquids; theoretically this appears to be correct, and the reasonableness of the results obtained may be considered a practical confirmation of their applicability.

UNIVERSITY COLLEGE,
CARDIFF.

CV.—*Phenol* p-*Sulphoxide.*

By Samuel Smiles and Alexander William Bain.

Some years ago Schall and Uhl (*Ber.*, 1892, **25**, 1893) prepared the dye-stuff rubbadin by heating together iodoform and sodium phenyl sulphite. These investigators further showed that rubbadin is decomposed by the action of fused caustic alkalis into salicylic acid and a compound containing sulphur.

The constitution of the dyestuff being unknown, the latter decomposition product is of some importance since the proof of its structure would indicate the nature and position of the sulphur group. Schall and Uhl inferred from their experiments that the substance was phenol *p*-sulphoxide, but they were unable to obtain clear proof of this structure since at that time no reaction was known by which the thionyl group could be detected. It is this uncertainty which has led us, as a preliminary to the study of the above product, to examine the synthetical sulphoxide.

The action of thionyl chloride on phenol was investigated by Tassinari (*Gazzetta*, 1890, **20**, 363), who found phenol sulphide to be the chief product; later, one of the present authors and Le Rossignol (Trans., 1906, **89**, 696) showed that, under suitable conditions, triphenolsulphonium chloride is alone formed. In the present paper it is shown that by adopting conditions similar to those described in the preparation of phenetyl sulphoxide (Smiles and Le Rossignol, *loc. cit.*), it is possible to obtain an almost theoretical yield of phenol *p*-sulphoxide.

We consider the constitution of the synthetical product to be proved by the facts:

(1) That it may be oxidised to phenol *p*-sulphone.

(2) That the action of ethyl iodide and alkali hydroxide yields *p*-phenetyl sulphoxide.

(3) That it yields sulphonium bases when treated with phenols or phenolic ethers in presence of a dehydrating agent.

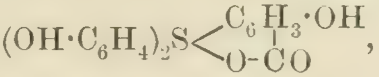
The first two reactions show the hydroxyl to be in the para-position to the sulphur, whilst the third indicates the thionyl group.

In the following table the properties of this substance and the derivatives which we have prepared are contrasted with those given by Schall and Uhl for their decomposition product of rubbadin:

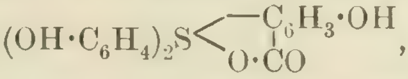
Source.	Phenol.	Acetyl Derivative.	Benzoyl Derivative.
Sch. and U...	Greyish-yellow sandy powder, m. p. 95·5°.	Greyish-yellow powder, m. p. 110·5°.	—
S and B........	Colourless needles, m. p. 195°.	Colourless needles, m. p. 84·5°	Colourless needles, m. p. 172°.

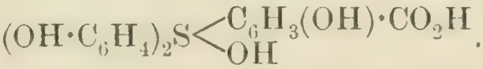
So far as can be judged from a comparison of this nature, the substances are different, but since it is possible that Schall and Uhl's preparation was not pure, we intend to investigate this question more fully.

The interaction of phenol *p*-sulphoxide and salicylic acid in presence of acid dehydrating agents yields the salt of a thetine, an aromatic analogue of the substances investigated by Crum Brown and Letts (*Trans. Roy. Soc. Edin.*, 1878, 28, 571). When the thetine salt is treated with alkali hydroxide or carbonate, the free thetine,



$$(OH\cdot C_6H_4)_2S<\begin{matrix}C_6H_3\cdot OH\\ |\\ O\text{-}CO\end{matrix},$$

is formed; this substance is neutral to litmus, and, like the fatty thetines, combines with one molecule of water, which can only be removed with difficulty. It is therefore doubtful whether the thetine should be written as  $(OH\cdot C_6H_4)_2S<\begin{matrix}C_6H_3\cdot OH\\ |\\ O\cdot CO\end{matrix}$, H_2O or



$$(OH\cdot C_6H_4)_2S<\begin{matrix}C_6H_3(OH)\cdot CO_2H\\ OH\end{matrix}.$$

The Action of Thionyl Chloride on Phenol. Phenol p-*Sulphoxide* $(C_6H_4\cdot OH)_2SO$.

Twenty-five grams of thionyl chloride were added gradually from a dropping funnel to an ice-cold solution of 25 grams of aluminium chloride and 45 grams of phenol in carbon disulphide. After each addition of thionyl chloride the mixture was well shaken, and the reaction which ensued was allowed to subside before a fresh portion of the acid chloride was introduced. When all had been added, the viscous mass was set aside for one hour and then decomposed with powdered ice; finally, carbon disulphide and unattacked phenol were removed by distillation in a current of steam. The contents of the flask were cooled and the acid liquid decanted from the solid material. The residue was crystallised from hot water, the sulphoxide separating as a flocculent, crystalline precipitate. The yield was 30—35 grams. Analysis of the dried substance furnished the following numbers:

0·1118 gave 0·2529 CO_2 and 0·0415 H_2O. C = 61·69; H = 4·12.
0·2137 ,, 0·2156 $BaSO_4$. S = 13·85.
$C_{12}H_{10}O_3S$ requires C = 61·54; H = 4·27; S = 13·67 per cent.

Phenol *p*-sulphoxide is sparingly soluble in hot water, but extremely soluble in alcohol or acetone; from the latter solvent it separates in short needles which melt at 195°. The substance also dissolves readily in concentrated sulphuric acid, giving solutions showing a deep Prussian blue colour which is removed by the addition of phenol, the salt of a sulphonium base being formed.

The *diacetyl* derivative was prepared by the interaction of the sulphoxide and acetyl chloride. It separates from hot alcohol in fine needles which melt at 84—85°:

0·1306 gave 0·2913 CO_2 and 0·0520 H_2O. C = 60·8; H = 4·4.
$C_{16}H_{14}O_5S$ requires C = 60·5; H = 4·4 per cent.

The *dibenzoyl* derivative was obtained by benzoylation of the sulphoxide in presence of alkali. It separates from hot alcohol in slender needles which melt at 172°:

0·2608 gave 0·6715 CO_2 and 0·0952 H_2O. C = 70·2; H = 4·0.
$C_{26}H_{18}O_5S$ requires C = 70·6; H = 4·0 per cent.

Oxidation of Phenol p-*Sulphoxide.*

The sulphoxide was dissolved in excess of aqueous alkali hydroxide, and a slight excess of powdered potassium permanganate was added gradually to the solution. The mixture was warmed on the water-bath, and the precipitated oxides of manganese were removed by filtration. Finally, the filtrate was acidified with dilute sulphuric acid and concentrated by evaporation, when a crystalline precipitate separated. This was recrystallised from dilute alcohol, collected, and dried; it then melted at 238—239°.

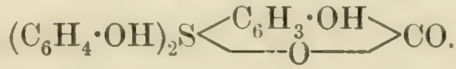
Phenol *p*-sulphone melts at 239° (Annaheim, *Ber.*, 1876, **9**, 1149); a sample was mixed with the above product, and the mixture was found to melt at 238—239°. Hence this sulphoxide on oxidation yields phenol *p*-sulphone.

Action of Ethyl Iodide on Phenol p-*Sulphoxide.*

Excess of ethyl iodide was added to a solution of the sulphoxide in alcoholic sodium hydroxide, and the mixture was heated for two hours on the water-bath. It was then evaporated to half its bulk and diluted with water. The precipitate which formed was filtered, washed first with aqueous sodium hydroxide and then with water, and was finally recrystallised several times from hot alcohol. The product melted at 115°, and when mixed with a sample of *p*-phenetyl sulphoxide

(m. p. 115—116°, Smiles and Le Rossignol, *loc. cit.*) melted at the same temperature.

Condensation of Phenol p-*Sulphoxide with Salicylic Acid : Di*-p-*hydroxyphenylsalicylthetine*, $(C_6H_4{\cdot}OH)_2S\Big\langle\begin{matrix}C_6H_3{\cdot}OH\\O\end{matrix}\Big\rangle CO$.



$$(C_6H_4{\cdot}OH)_2S\Big\langle\begin{matrix}C_6H_3{\cdot}OH\\O\end{matrix}\Big\rangle CO$$

An intimate mixture of the sulphoxide and salicylic acid in molecular proportions was added to about four times its weight of concentrated sulphuric acid. After remaining at the ordinary temperature for half an hour, the green solution was poured into water, when a colourless precipitate of the thetine sulphate separated. This was collected and warmed in aqueous alcoholic solution with barium hydroxide to remove sulphuric acid. The filtrate from the barium sulphate was saturated with carbon dioxide and again filtered. Water was then added to the clear solution to precipitate the thetine, which was purified by reprecipitation from aqueous alcohol. In this way *di*-p-*hydroxyphenylsalicylthetine* was obtained as a colourless solid melting at 212°. It is insoluble in water, but dissolves in hot alcohol, giving a solution which shows a neutral reaction with litmus, and which gives no coloration on the addition of aqueous ferric chloride.

The air-dried substance was heated to constant weight at 108°:

0·1390 lost 0·0064 H_2O. $H_2O = 4·6$.

$C_{19}H_{16}O_6S,H_2O$ requires $H_2O = 4·6$ per cent.

The product dried at this temperature was analysed with the following results:

0·1149 gave 0·2589 CO_2 and 0·0436 H_2O. $C = 61·4$; $H = 4·2$.

$C_{19}H_{16}O_6S$ requires $C = 61·3$ and $H = 4·3$ per cent.

When heated at 130° for some time, the substance lost a further quantity of water. Thus:

0·2444 (dried at 105°) lost 0·0118 H_2O (at 130°). $H_2O = 4·8$.

$C_{19}H_{16}O_6S$ on passing to $C_{19}H_{14}O_5S$ requires $H_2O = 4·8$ per cent.

The *platinichloride* was obtained as a salmon-coloured powder melting at 182—183°. After being dried at 100°:

0·1125 gave, on ignition, 0·0192 Pt. $Pt = 17·06$.

$(C_{19}H_{15}O_5ClS)_2,PtCl_4$ requires $Pt = 17·4$ per cent.

In conclusion, the authors desire to express their hearty thanks to Professor Collie for the interest he has taken in the above experiments.

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CVI.—*The Relation between Absorption Spectra and Chemical Constitution. Part VII. Pyridine and some of its Derivatives.*

By FRANK BAKER and EDWARD CHARLES CYRIL BALY.

THE object of the present investigation was to study the effect of the replacement of a CH group of the benzene ring by the N atom as in the pyridine compounds, for the nitrogen atom possesses a different type of unsaturation from that of a carbon atom. It has been previously shown (Baly and Collie, Trans., 1905, 87, 1332) that the substitution of one of the hydrogen atoms of benzene by an atom or group of atoms possessing residual affinity modifies the absorption spectrum to a very marked degree.

The spectra of pyridine, picoline, and piperidine have already been observed by Hartley (Trans., 1885, 47, 685). The two former spectra are of the same type as those of the benzene hydrocarbons in that they show broad absorption bands. The latter compound, on the other hand, shows only continuous absorption in the ultraviolet, thus proving that, as in the case of *cyclo*hexane which has been investigated by Hartley and Dobbie (Trans., 1900, 77, 846), the formation of the saturated compound eliminates the absorption band.

The curves obtained by Hartley for pyridine are shown in Fig. 1. We have re-examined the absorption spectra of pyridine and the picolines, and find substantially the same results as Hartley. We have examined 2:6-lutidine, and the absorption curves are given in Fig. 1. It is evident from these curves that there is a considerable amount of tautomerism of the benzenoid type present in the case of these compounds. The effect of the introduction of methyl groups into pyridine is not to alter the character of the band, but to move it slightly towards the red, and at the same time to decrease the persistence. The oscillation frequencies of the heads of the bands are shown below:

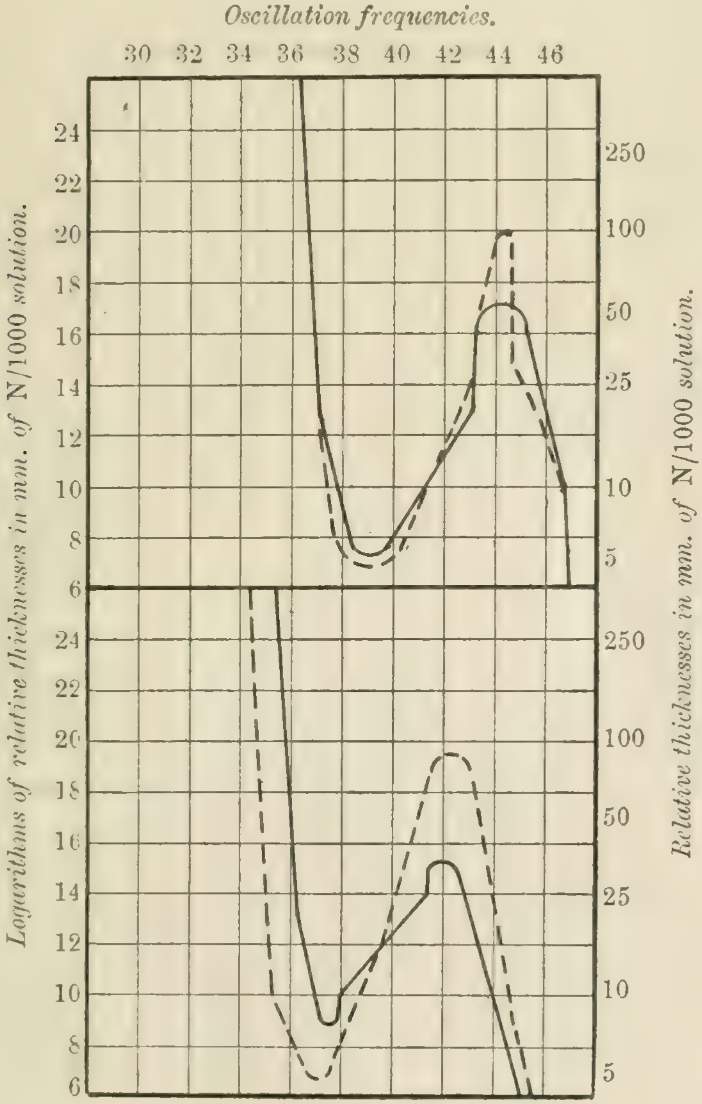
Pyridine...............	3950 (Hartley)
α-Picoline	3875
β-Picoline	3800
Lutidine...............	3750

The effect of the addition of hydrochloric acid to the solutions of these compounds is very striking, as can be seen on reference to the dotted curves in Fig. 1.

In each case the persistence of the absorption band has been greatly increased.

In the case of benzene it is found that the introduction of a group possessing considerable residual affinity tends to stop the vibration of the benzene ring. These results go to show that in pyridine the same effect is produced by the residual affinity of the nitrogen atom. By the addition of the hydrochloric acid this residual affinity is, to a large extent, satisfied and the restraining influence at the same time removed.

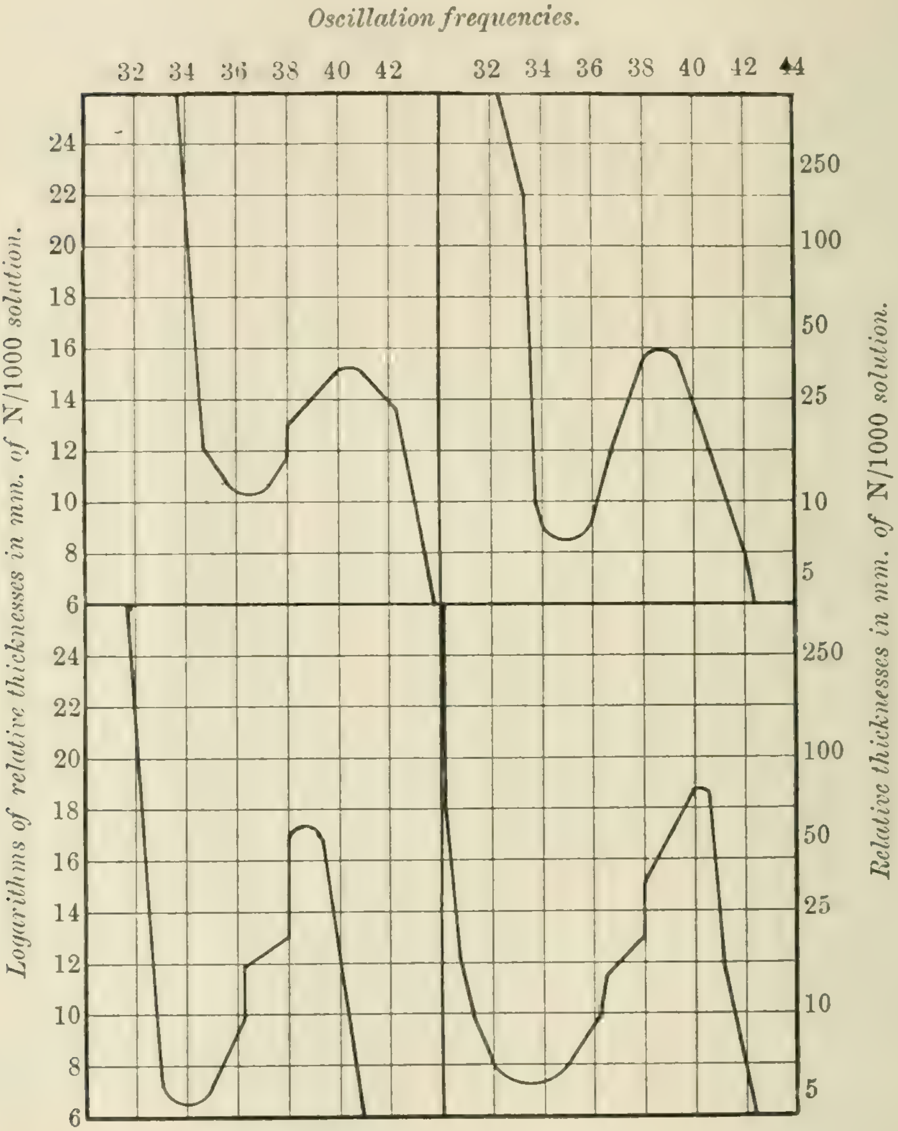
FIG. 1.



Upper curves : *Pyridine* (Hartley).
Lower ,, 2 : 6-*Lutidine.*
Full curve : *Free base.*
Dotted ,, *Hydrochloride.*

The tautomeric process is thus increased, as shown by the increased persistence of the absorption band. Thus important support is given by these observations to the hypothesis that the so-called benzenoid tautomerism is due to the ring being in a state of vibration or pulsation (Baly, Edwards, and Stewart, Trans., 1906, **89**, 514). In the case of the free pyridine compounds the tendency to pulsate is restrained by the unsaturation of the nitrogen atom, and the removal of this influence by the addition of hydrochloric acid allows greater freedom to the ring pulsation. It is interesting to note that the broad band of pyridine is not resolved into smaller bands like those of benzene when in hydrochloric acid solution. In this respect it differs to a marked extent from that of aniline (Baly and Collie, *loc. cit.*). This indicates that there is a great difference between the nitrogen and carbon atoms in the amount and nature of their residual affinity. In no case in the

Fig. 2.



I. 3 : 4 : 5-*Trichloropyridine*. II. 2 : 3 : 4 : 5-*Tetrachloropyridine*.
III. *Pentachloropyridine*. IV. 1-*Methyl-2-pyridone*.

compounds of pyridine examined is it possible to sub-divide the broad absorption bands into smaller bands.

The absorption spectra of certain chlorine substituted derivatives have also been investigated. The absorption curves of 3 : 4 : 5-trichloropyridine, 2 : 3 : 4 : 5-tetrachloropyridine, and pentachloropyridine are shown in Fig. 2.

The positions of the heads of the bands are as follows, expressed in oscillation frequencies :

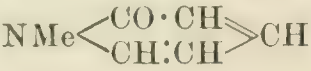
Trichloropyridine	3650
Tetrachloropyridine	3500
Pentachloropyridine	3400

It is thus apparent that the introduction of chlorine produces a gradual shift of the band towards the red ; at the same time the persistence of the band, as may be seen on reference to the curves, is greatly increased. The latter effect may be explained by the fact that the introduction of chlorine into the molecule reduces the residual affinity of the nitrogen atom. This is in agreement with the chemical properties of these compounds, for it is well known that the basicity of pyridine is materially decreased by the substitution of the hydrogen atoms by chlorine.

At the same time, the loading of the ring by the introduction of the heavy chlorine atoms retards the free period of the vibration, the absorption band thus being shifted towards the red. This is similar to the effect observed by Hartley in the general case of substituted compounds. He found that the higher the molecular weight of the group introduced into the molecule, the greater the shift of the absorption band towards the red end of the spectrum.

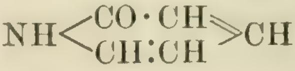
The absorption spectra of the three pyridones have also been examined. The curves obtained are shown in Figs. 3, 4, and 5.

In Fig. 3 the absorption spectra of α-pyridone in neutral, acid, and alkaline solution are given. In neutral solution there is exhibited an absorption band with head situated at an oscillation frequency of 3300, which is considerably removed from the head of the band of pyridine. The effect of the addition of hydrochloric acid is merely to cause a slight shift of the band towards the ultra-violet, whilst the persistence of the band is not changed. In presence of alkali (sodium ethoxide) the band is only slightly narrowed, no shift towards the red taking place. This indicates that the tautomerism is not of a phenolic nature, since in such a case the band would be shifted towards the red (Baly and Ewbank, Trans., 1905, 87, 1347). The resemblance of these spectra to that of the 1-methyl-2-pyridone, Fig. 2, which undoubtedly has the formula (I) in conjunction with the action of acid, and alkali on the pyridone itself prove that α-pyridone exists practically entirely in the ketonic form (II):



$$\mathrm{NMe}<\begin{matrix}\mathrm{CO\cdot CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH}$$

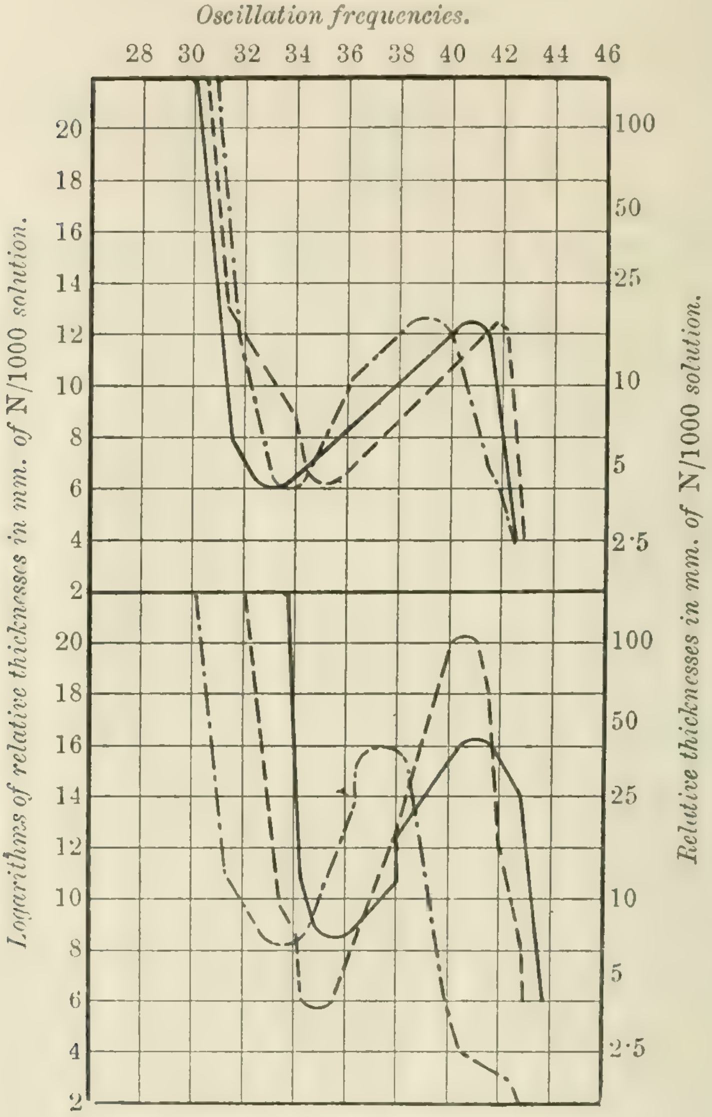
(I.)



$$\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH}$$

(II.)

FIG. 3.



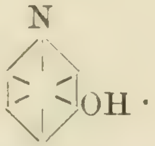
Upper curves : *α-Pyridone.*
Lower ,, *β-Pyridone.*

Full curve : *Pyridone.*
Dotted ,, ,, *with* HCl.
Dot and dash curve : *Pyridone with* NaOEt.

The tautomerism to which the absorption band is due therefore must take place between the carbonyl group and the double linkings shown in the formula, and cannot be due to the same process as occurs in pyridine. This will explain the fact that, unlike the compounds of pyridine already described, the satisfaction of part of the residual affinity of the nitrogen atom by the addition of hydrochloric acid does not increase the persistence of the band. Furthermore, the unusually small value of the oscillation frequency of the head of the band is also accounted for.

In Fig. 3 the full, dotted, and dot and dash curves show the absorption spectra of β-pyridone in neutral, acid, and alkaline solutions respectively, and, as can be seen, they are very different from those of α-pyridone. The effect of the addition of hydrochloric acid is to increase very materially the persistence of the absorption band as in the case of pyridine and the methyl derivatives described above. The addition of sodium ethoxide, however, causes a shift of the band towards the red, whilst the persistence of the band is not affected. There is thus considerable analogy to the phenols (Baly and Ewbank, *loc. cit.*).

We may therefore conclude that in the case of β-pyridone the substance undoubtedly exists chiefly in the hydroxyl form, that is, β-pyridone has the formula:



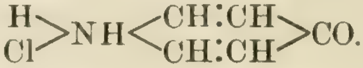
It may be pointed out in support of this conclusion that the position of the absorption band in this substance, both in neutral and acid solution, is almost identical with that of the phenols.

The case of γ-pyridone is peculiarly interesting, its curves being shown in Fig. 4. In neutral solution the substance shows an absorption band which is entirely removed by sodium ethoxide. This at once shows an entire difference from the β-isomeride.

Compounds of the type of acetone, namely, mono-ketones with a carbonyl group situated between two carbon atoms, show evidences of tautomerism (Stewart and Baly, Trans., 1906, **89**, 489), and they are very sensitive to the presence of alkali hydroxides or even water; moreover, the tautomerism is decreased to an extraordinary degree, owing no doubt to the association of the water or sodium hydroxide with the carbonyl group. It would thus seem that γ-pyridone is analogous, that is to say, it is mainly in the form

$$NH<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CO.$$

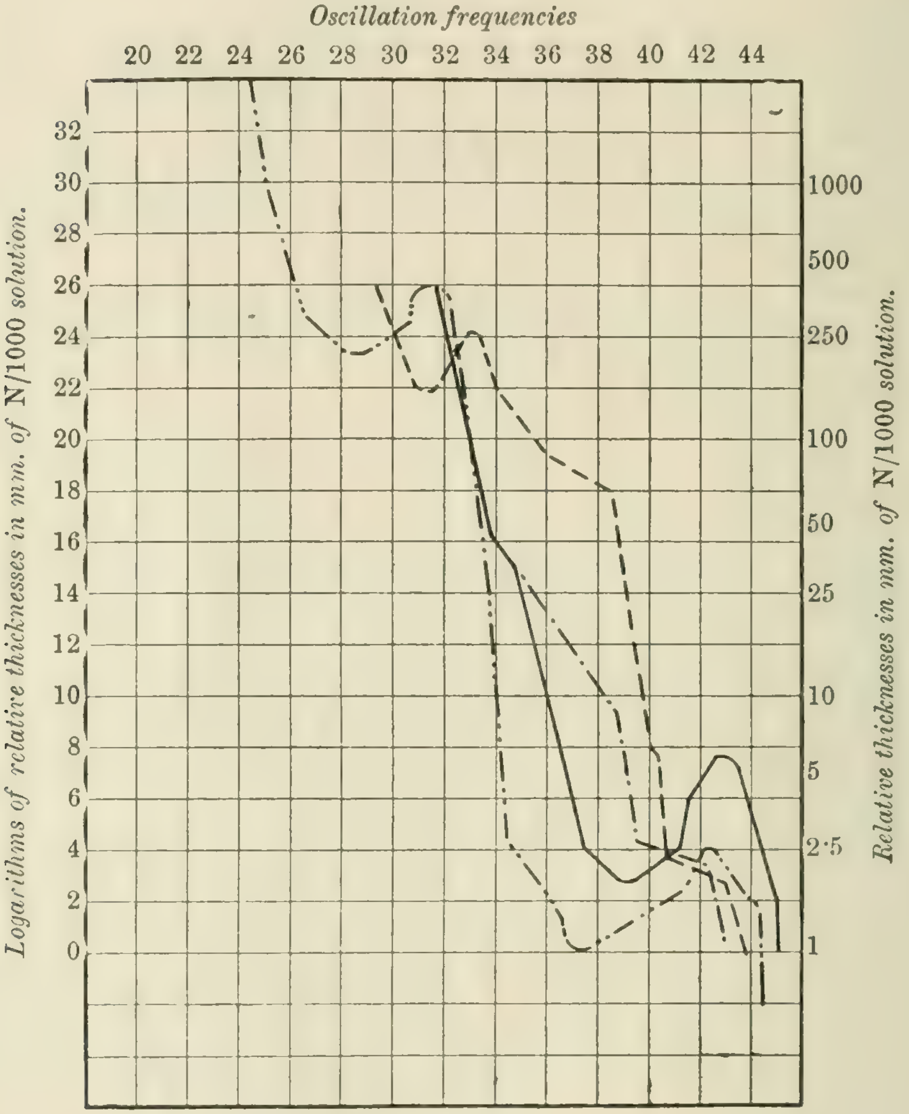
This conclusion is strikingly confirmed by the curve of absorption obtained in presence of hydrochloric acid. As with sodium ethoxide, the tautomerism has certainly ceased, but a new band has appeared at greater concentration and much nearer the red end of the spectrum. This band is evidently due to a process of isorropesis and not to simple tautomerism. Owing to the formation of the hydrochloride, the addition of hydrochloric acid to γ-pyridone should tend to lock it in the form



$$\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\!>\mathrm{NH}<\!\begin{matrix}\mathrm{CH{:}CH}\\\mathrm{CH{:}CH}\end{matrix}\!>\mathrm{CO}.$$

This formula contains a CO group between two ethylenic linkings,

FIG. 4.



Full curve : *γ-Pyridone.*
Dash and dot curve : *γ-Pyridone in* NaOEt.
Dotted ,, ,, ,, HCl.
Dash and two dots curve : *Phorone.*

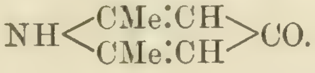
and as such a grouping should give rise to a process of isorropesis we should obtain a new absorption band. To decide this point, the absorption spectrum of phorone,

$$\mathrm{CMe_2{:}CH{\cdot}CO{\cdot}CH{:}CMe_2},$$

in which a similar linking occurs, was observed and is shown by the dash and two dots curve in Fig. 4. It is noticeable that in phorone a very similar band occurs.

The conclusions drawn from the absorption spectra of the pyridones are borne out by their behaviour with methyl iodide and sodium. In the cases of the α-pyridone the 1-methyl compound is easily obtained, whilst in the case of β-pyridone the methiodide on treatment with alkali loses methyl iodide, the 1-methyl derivative not being formed in this way. A ketonic pyridone on treatment with methyl iodide would give a compound containing the group $>NH\left<\begin{matrix}CH_3\\I\end{matrix}\right.$, from which alkalis would readily remove hydrogen iodide. A hydroxy-compound, on the other hand, would give $\left.\begin{matrix}{:}CH\\ \cdot CH\end{matrix}\right\geqslant N\left<\begin{matrix}CH_3\\I\end{matrix}\right.$, which would not readily lose hydrogen iodide.

The absorption spectrum of γ-lutidone was also observed in neutral, acid, and alkaline solution. The curves obtained are shown in Fig. 5, and are found to be similar to those of γ-pyridone. This, of course, was to be expected from the similarity of the properties of the two compounds, hence we may conclude that the lutidone has the formula



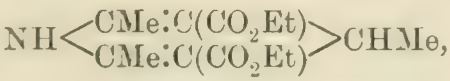
$$NH\left<\begin{matrix}CMe{:}CH\\CMe{:}CH\end{matrix}\right>CO.$$

The absorption spectrum of γ-ethoxylutidine has also been determined, and, as will be seen on reference to the curve, Fig. 5, no absorption band is produced. The addition of acid, even to 60 equivalents, has also no effect on this spectrum.

It may be pointed out that although the α- and γ-pyridones both possess the ketonic configuration, yet their absorption curves are different in type. In the latter compound the carbonyl group is situated between two unsaturated carbon atoms, whilst in the former the carbonyl group is adjacent to an NH group. We should therefore expect, as is the case, that the γ-derivative would conform to the type of a mono-ketone, but that the α-compound would not.

Interesting results have also been obtained from the examination of certain more complicated derivatives of pyridine.

Ethyl 2 : 4 : 6-trimethyl-Δ^2-dihydropyridine-3 : 5-dicarboxylate was first examined. This compound, which possesses the formula



$$NH\left<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}\right>CHMe,$$

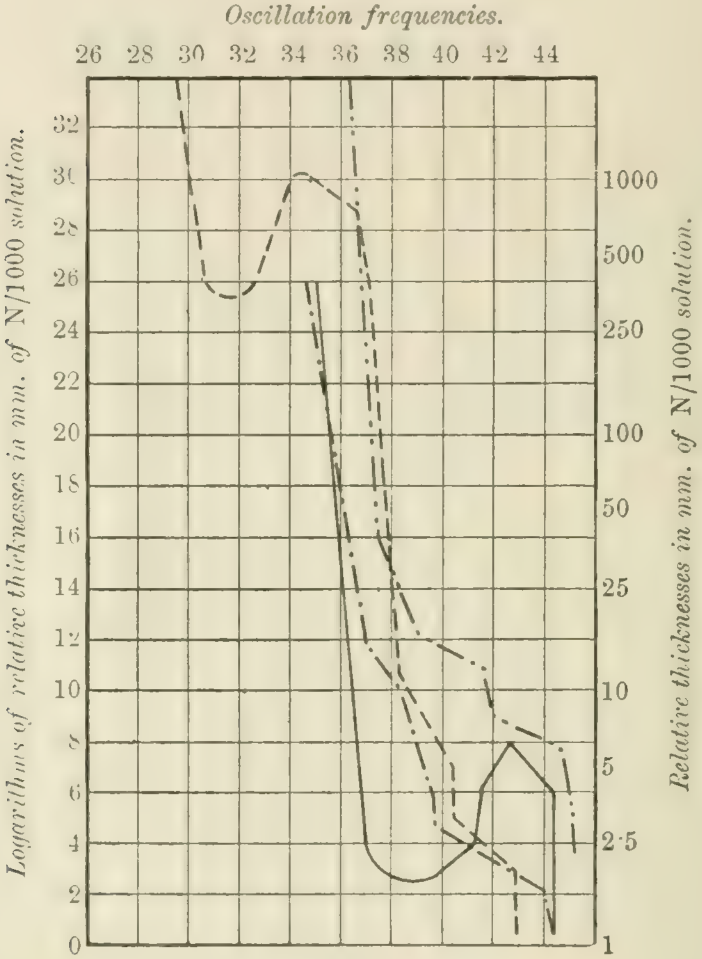
shows a blue fluorescence both in the solid state and in alcoholic solution.

The curve of absorption is given in Fig. 6, and shows a band of frequency 2950 with extremely great persistence.

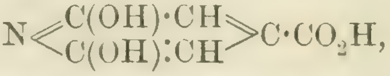
The formula, however, includes two CO groups adjacent to double linkings, and undoubtedly the combined effects of this produce a type of isorropesis to which this absorption band is due.

The next compound studied was citrazinic acid. As the substance was insoluble in water and alcohol, a solution was prepared by shaking the finely-powdered substance with a decinormal solution of sodium hydroxide, with exclusion of air. The solution exhibited a brilliant blue fluorescence, even when diluted to $N/10,000$. The curve obtained is shown in Fig. 6, and is almost precisely the same as that of the previous compound. The formula of citrazinic acid is

Fig. 5.



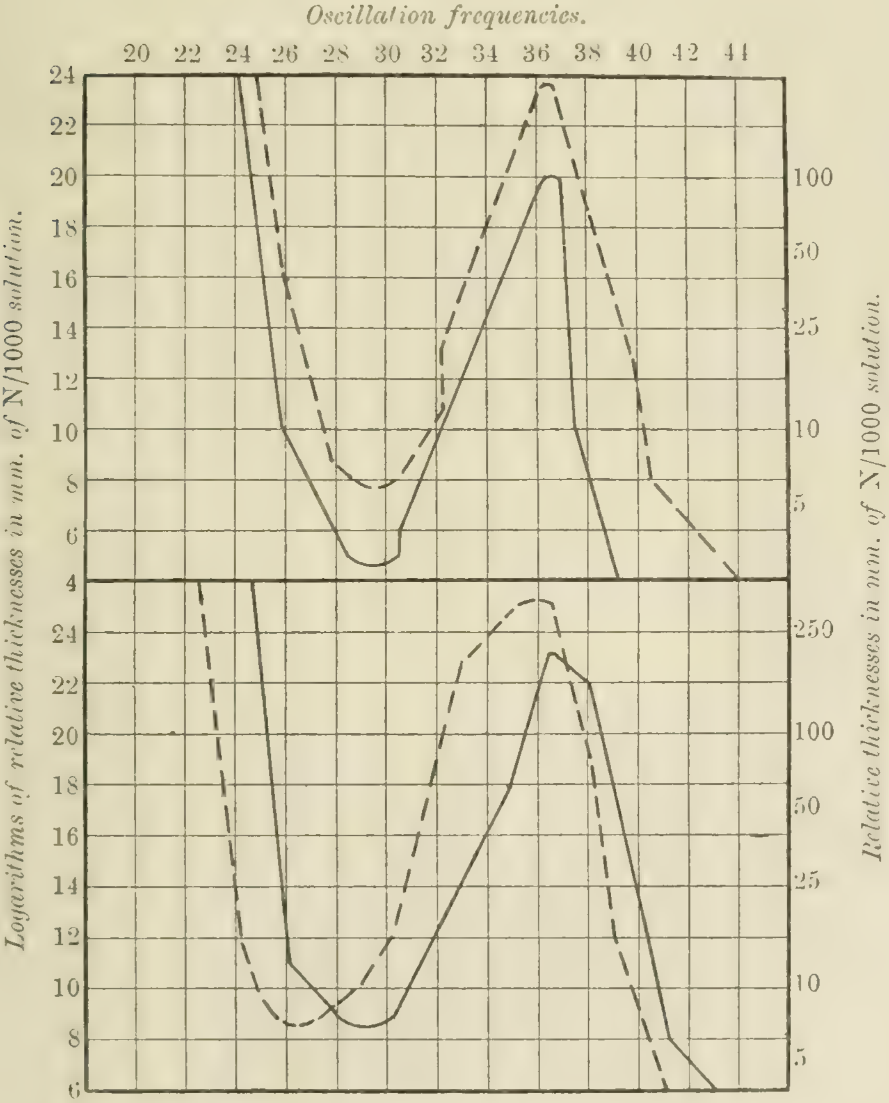
Full curve: γ-*Lutidone.*
Dotted „ „ *with* HCl.
Dash and dot curve: γ-*Lutidone with* NaOEt.
Dash and two dots curve: γ-*Ethoxylutidine.*



$$\mathrm{N}\!<\!\begin{matrix}\mathrm{C(OH)\cdot CH}\\ \mathrm{C(OH):CH}\end{matrix}\!>\!\mathrm{C\cdot CO_2H},$$

and as it is obvious that there are several possibilities of tautomerism in the hydroxyl groups, it is undoubtedly to this, together with the resulting conjugation and isorropesis, that we can attribute the remarkable absorption band. We have found undoubted evidence of the existence of this type of phenolic tautomerism in the case of the ethyl ester of citrazinic acid. The absorption curves of this substance in neutral and alkaline solution are shown in Fig. 6. The shift of the absorption band towards the red in alkaline solution, characteristic of phenols, is clearly marked. This also agrees with the statement of Hofmann and Behrmann (*Ber.*, 1884, **17**, 2691) that citrazinic ester behaves as an acid.

FIG. 6.



Upper curves –
Full curve : *Trimethyldihydropyridinedicarboxylic ester.*
Dotted ,, *Sodium salt of citrazinic acid.*

Lower curves—
Full curve : *Citrazinic ester.*
Dotted ,, ,, ,, *with* NaOEt.

EXPERIMENTAL.

In the case of each compound described above, precautions were taken to ensure the purity of the substances employed.

In the case of the free bases, pyridine, and the methyl derivatives, the compounds were prepared from recrystallised specimens of their salts with mercuric chloride. These substances all possessed the correct melting points.

The pyridones were, in the case of compounds, purified by crystallisation from a small quantity of water; pyridone was obtained pure and colourless by redistillation. The three compounds all melted at the correct temperature.

Specimens of the pure chlorine derivatives were very kindly given us by Dr. W. J. Sell, and for the ethoxylutidine, γ-lutidone, and γ-pyridone we are indebted to Prof. J. N. Collie. Citrazinic acid was obtained pure by the method described by Hofmann and Behrmann (*loc. cit.*), whilst the ester of this acid and also of trimethyldihydropyridinedicarboxylic acid were recrystallised several times from alcohol.

Conclusions.

1. Pyridine, the picolines, and 2 : 6-lutidine show evidence that the benzenoid tautomerism is restrained by the unsaturated nature of the nitrogen atom.

2. This restraint is removed on the addition of hydrochloric acid and the tautomerism is greatly increased. Assuming that the tautomerism is due to the pulsation of the ring, we may conclude that this process does not take place in pyridine or its homologues with a freedom comparable to that in benzene, but that owing to the residual affinity of the nitrogen atom a powerful restraint is exercised. The partial removal of this restraint by the addition of hydrochloric acid allows much greater freedom to the motions of the ring.

3. An effect quite analogous to that given by hydrochloric acid is produced by the substitution of the hydrogen atoms of pyridine by chlorine atoms.

4. In the case of the pyridones, the α- and γ-compounds have the ketonic constitution, whilst the β-isomeride is a true hydroxy-derivative.

We wish to express our thanks to Prof. Collie for the interest he has taken in this paper, and to the Chemical Society for a grant in aid of the work.

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CVII.—*Oxime Formation and Decomposition in Presence of Mineral Acids.*

By Arthur Lapworth.

During the study of certain cyclic ketones, some compounds, supposed to be *iso*nitrosoketones or diketonemonoximes, displayed a high degree of stability, and could not be converted into the corresponding diketones by any of the usual methods, so that a more effectual mode of replacing the *iso*nitroso-group by oxygen than any now in general use was therefore sought.

The most unstable oximes can be resolved into hydroxylamine and ketone or aldehyde by means of dilute mineral acids, and in extreme cases even by alkalis. In other instances these methods are not successful, as, for example, in the case of *iso*nitrosocamphor, and recourse must be had to the use of nitrous acid or bisulphite, in which cases the hydroximino-group is oxidised or reduced respectively. The use of nitrous acid is often precluded by the nature of the rest of the molecule, and both agents fail altogether in at least one instance, namely, that of camphoroxime, which has only been indirectly resolved (compare Forster, Trans., 1897, **71**, 199).

Forster obtained camphorquinone from *iso*nitrosocamphor by converting the latter into its *N*-methyl derivative, which, with acids, furnishes the quinone together with β-methylhydroxylamine (Trans., 1904, **85**, 896), but this method appears to be, if anything, less generally applicable than the others.

The compound chosen for preliminary experiments was *iso*nitrosocamphor, which is convenient because, whilst it is colourless or nearly so, the ketone from which it is derived, namely, camphorquinone, is bright yellow. It was observed that, when the *iso*nitroso-compound was warmed with dilute mineral acid, a faint yellow tinge was quickly developed, but never became intense. It was thought possible that this might be due to a slight reversible decomposition into ketone and hydroxylamine, and if so, the introduction of ketones or aldehydes, which are more reactive than camphorquinone, would possibly increase the effect. It was found that most ketones and chloral produced little or no effect, but that benzaldehyde, acetaldehyde, and more especially formaldehyde caused a decided augmentation of the yellow tint. With the conditions at first employed, further action soon ceased, as was to be anticipated, for it is well known that the oximes of these compounds are largely decomposed by dilute acids into their generators. The effect of a large excess of formaldehyde was investigated, but, although the colour was thereby further intensified, no camphorquinone could be isolated.

Before abandoning the idea, however, another series of experiments was tried with concentrated hydrochloric acid. In this, using formaldehyde, rapid change occurred, and crystals of the quinone separated within a few minutes. Further trial proved that this method provides perhaps the cheapest and most rapid method of preparing camphorquinone, the yield obtained being from 70—85 per cent. of the theoretical. (The following gives about 75 per cent.)

*iso*Nitrosocamphor (15 grams) is warmed for half an hour on the water-bath with 40 per cent. formaldehyde (15 c.c.) and two drops of concentrated sulphuric acid. At the end of this time, concentrated hydrochloric acid (30 c.c.) is added and the heating continued until the deposited oil becomes nearly solid. The quinone is then driven off in a current of steam.

The effect of formaldehyde in removing the hydroximino-groups of other ketoximes was examined. Solutions of acetophenoneoxime and benzophenoneoxime respectively in cold dilute acids were made, and formaldehyde was added to portions of the clear liquids, when immediate separation of insoluble material took place, and, on extracting the resulting liquids with ether, good yields of the free ketones were obtained without difficulty; the liquids to which no formaldehyde had been added remained clear throughout.

As a more severe test of the applicability of the method, camphoroxime, which is not resolved by any of the usual methods, was examined. Here it was certainly less successful, but apparently only because this oxime is so readily converted into derivatives of campholenonitrile in acid solution.

Camphoroxime (50 grams) and formaldehyde (50 c.c.) were mixed and heated with concentrated hydrochloric acid (150 c.c.) on the water-bath for one and a half hours, the product was then distilled in a current of steam and the camphoraceous distillate extracted with benzene. The extract was washed with water, dried, and distilled. From the fraction boiling between 195° and 230° some grams of camphor separated, but the whole was shaken with a cold solution of potassium permanganate to remove campholenonitrile, and, when further change ceased, the manganese dioxide was dissolved by means of a stream of sulphur dioxide, and the suspended camphor separated by filtration, dried, and sublimed; 7·5 grams in a state of purity were obtained by this process.

With the view of testing whether the function of the formaldehyde in the above experiments was merely to remove any hydroxylamine formed by slight reversible hydrolysis of the oximes, further experiments were made. It was unlikely that the result depended merely on the production of formaldoxime, as this compound is much more easily hydrolysed by acids than are the oximes of camphor or camphorquinone, and Dunstan and Bossi (Trans., 1898, **73**, 359) have shown that, in presence of hydrochloric acid, formaldoxime may sometimes be converted into hydrogen cyanide, but in the experiments described above no trace of hydrogen cyanide could be detected.

Twenty-five grams of *iso*nitrosocamphor were decomposed by formaldehyde and hydrochloric acid as above described, and the residue, after steam distillation, was evaporated to dryness. On extracting with absolute alcohol, 3·3 grams of ammonium chloride were left undissolved, whilst from the alcoholic extract rather more than 1 gram of camphorimide, produced by isomeric change of the *iso*nitroso-compound, was isolated.

A second hydrolysis of the same amount of *iso*nitrosocamphor was then undertaken, but with pure methylal instead of formaldehyde, a blank experiment having shown that methylal and hydrochloric acid yield only a trace of formic acid. In this instance the liquor, before removal of camphorquinone, was rendered neutral by addition of sodium carbonate, and then distilled in a current of steam until only water passed over, when excess of dilute sulphuric acid was added and the steam distillation continued. Formic acid was detected without difficulty in the distillate, and on neutralising it with lead carbonate, filtering, and evaporating, the characteristic crystals of lead formate, weighing 9·5 grams, were obtained [Pb = 69·6 : $Pb(CHO_2)_2$ requires Pb = 69·7 per cent].

In order to ascertain how formaldehyde and hydroxylamine hydrochloride interact in presence of excess of concentrated hydrochloric acid, a solution of hydroxylamine hydrochloride (10 grams) in concentrated hydrochloric acid (50 c.c.) was mixed with formaldehyde (10 c.c.) and warmed. A somewhat violent reaction occurred and continued without the further application of external heat. At the end of two hours the whole was evaporated and a current of steam was passed over the residue until the odour of formaldehyde was no longer noticeable. The mass of salts left was extracted with absolute alcohol, when about 5 grams of ammonium chloride remained undissolved. The process of evaporation and extraction was repeated to remove dissolved ammonium chloride. By careful crystallisation of the most soluble portions from water, 2 grams of hydroxylamine hydrochloride were isolated and identified by the usual tests :

0·2402 required 34·7 c.c. N/10 $AgNO_3$. Cl = 51·3.

$NH_2{\cdot}OH,HCl$ requires Cl = 51·1 per cent.

The mother liquors from this salt contained a very soluble hydrochloride which, when warmed with strong alkali, gave off an inflammable gas; they were therefore rendered alkaline and fractionally distilled into hydrochloric acid, which was evaporated to dryness and the residue extracted with absolute alcohol. The salt which dissolved was easily identified as methylamine hydrochloride, and the platinichloride was analysed:

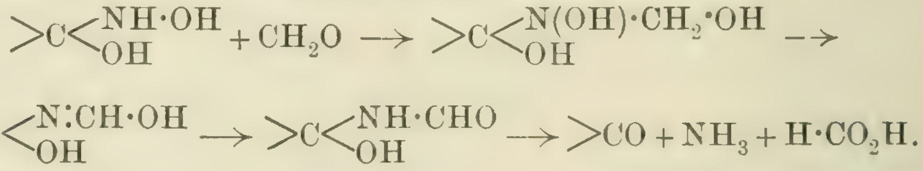
0·7120 gave 0·2926 Pt. Pt = 41·1.

$C_2H_{12}N_2Cl_6Pt$ requires Pt = 41·3 per cent.

The production of methylamine in this reaction recalls the method of preparing the methylamines by heating formaldehyde with ammonium chloride, but is even more striking, as a large excess of hydrochloric acid was present.

Hydroxylamine hydrochloride is therefore reduced by formaldehyde * in presence of concentrated hydrochloric acid; nevertheless a considerable quantity remains unaffected even in presence of excess of formaldehyde. It is thus not possible in all instances to attribute the action of formaldehyde and hydrochloric acid on the oximes to this circumstance, for it must be remembered that only a very small amount of hydroxylamine hydrochloride can be present in a solution of camphoroxime or *iso*nitrosocamphor in hot concentrated hydrochloric acid, otherwise camphor and camphorquinone respectively could easily be obtained by allowing these volatile substances to distil, especially with the aid of a current of steam, and this is not the case.

It seems more probable that, in presence of acid, the oximes reacting as hydroxyhydroxylamino-compounds combine with formaldehyde, the subsequent addition compound then undergoing a transformation analogous to the Beckmann change, yielding formic acid, ammonia, and ketone. The following may be suggested as plausible:



$$>C<\begin{matrix}NH\cdot OH\\ OH\end{matrix} + CH_2O \longrightarrow >C<\begin{matrix}N(OH)\cdot CH_2\cdot OH\\ OH\end{matrix} \longrightarrow$$

$$>C<\begin{matrix}N{:}CH\cdot OH\\ OH\end{matrix} \longrightarrow >C<\begin{matrix}NH\cdot CHO\\ OH\end{matrix} \longrightarrow >CO + NH_3 + H\cdot CO_2H.$$

In either case, however, it seemed necessary to conclude that oximes would be formed from aldehydes and ketones with hydroxylamine in presence of a large excess of concentrated mineral acids, and to test this supposition the following experiments were made.

A cold solution of acetophenoneoxime in concentrated hydrochloric acid was prepared and divided into two parts; to one of these, hydroxylamine hydrochloride was added and then both were warmed on the water-bath. The solution which contained excess of hydroxyl-

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* The oxidising effect of hydroxylamine in presence of concentrated hydrochloric acid has frequently been noticed (compare Biltz, *Ber.*, 1896, **29**, 2080). Nietzki and Kehrmann (*Ber.*, 1887, **20**, 614) found that quinol was converted by this agent into quinonedioxime.

amine hydrochloride remained clear for several hours and was afterwards found to contain unaltered oxime, whilst the other solution rapidly deposited acetophenone, and in a short time no unaltered oxime could be detected. Experiments with benzophenoneoxime gave similar results, so that it appears that the conversion of oximes into ketone and hydroxylamine by concentrated mineral acids is a reversible change.

Reaction between benzaldehyde and hydroxylamine in concentrated hydrochloric acid occurs with astonishing readiness. If a saturated solution of hydroxylamine hydrochloride in concentrated hydrochloric acid is warmed and shaken with a small quantity of benzaldehyde, the latter, at first insoluble, very rapidly disappears, and on cooling and pouring the liquid into a large bulk of water an oil separates. This is almost entirely α-benzaldoxime, as was proved by washing it, dissolving in ether, and converting it into benzaldoxime hydrochloride in the usual way. The hydrochloride melted at 66°, and on analysis:

0·2172 gave 0·2002 AgCl. Cl = 22·8.

$C_6H_5 \cdot CH\colon N \cdot OH,HCl$ requires Cl = 22·5 per cent.

Under certain conditions, benzaldehyde, when heated with a solution of hydroxylamine hydrochloride in concentrated hydrochloric acid, dissolves, and the resulting solution subsequently becomes milky owing to the conversion of the benzaldoxime into benzonitrile, the identity of which was satisfactorily established by the usual physical and chemical tests.

Camphorquinone, when heated on the water-bath with excess of a saturated solution of hydroxylamine hydrochloride in concentrated hydrochloric acid, dissolves slowly giving a nearly colourless solution which on evaporation leaves an oil. This when washed, dried, and distilled, yields a crystalline compound which was easily identified as camphorimide. This substance is produced from *iso*nitrosocamphor by the action of acids, and its formation here indicates that the camphorquinone is converted into its oxime, although the latter could not actually be isolated.

Camphor, dissolved in a little alcohol and heated with concentrated hydrochloric acid saturated with hydroxylamine hydrochloride, is very slowly changed; the product from one experiment, during which the heating had been continued for some days, was distilled with steam. The distillate, which had the odour of raspberries, was extracted with ether and the extracted matter distilled. A considerable quantity of camphor was recovered, but a fraction was obtained which contained nitrogen and had a distinct odour of raspberries; it decolorised solutions of bromine and potassium permanganate at once in the cold, and had all the characters of campholenonitrile although it could not be obtained quite free from dissolved camphor; its formation establishes the fact that camphoroxime was formed to some extent in the initial stages of the above reaction.

Although there are instances of the use of hydroxylamine in presence of acids in the preparation of oximes to be found in the literature (compare Nietzki and Kehrmann, *Ber.*, 1887, **20**, 614, and Schunck and Marchlewski, *ibid.*, 1894, **27**, 3464), that the reaction is a general one and takes place so readily in presence even of concentrated hydrochloric acid does not appear to be recognised.

A subsequent communication will deal with some measurements of the velocity of reaction of hydroxylamine with acetone and with aldehyde in presence of varying quantities of bases and acids, both of which, it may be stated, have been found to cause acceleration.

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CVIII.—*Dibromoaminoazobenzene.*

By JOHN THEODORE HEWITT and NORMAN WALKER.

IN a number of communications presented to the Society (Trans., 1900, **77**, 99, 712, 810; 1901, **79**, 49, 155, 160, 1090; 1902, **81**, 171, 1202; 1905, **87**, 225; 1906, **89**, 182) it has been shown that hydroxyazo-compounds, when submitted to the action of substituting agents such as nitric acid or bromine, regularly behave as azophenols rather than as quinonehydrazones, except in such cases where the non-hydroxylated aromatic nucleus has a free para-position and the substance is not protected against the action of strong mineral acids. In the simplest case, that of benzeneazophenol, bromine acts on the substance in glacial acetic acid solution, giving *p*-bromobenzeneazo-*o*-*o*-dibromophenol when no precautions are observed to protect the substance against the influence of the hydrogen bromide liberated during the reaction, whilst if fused sodium acetate be also present, then benzeneazo-*o*-*o*-dibromophenol may be obtained in nearly quantitative yield. Similarly, *p*-nitrobenzeneazophenol is obtained on dissolving benzeneazophenol in an excess of concentrated sulphuric acid and adding one molecular proportion of nitric acid, whilst on warming benzeneazophenol with dilute nitric acid a fair yield of benzeneazo-*o*-nitrophenol is produced.

Despite these numerous experiments with hydroxyazo-compounds, the aminoazo-compounds have been but little examined with regard to their behaviour towards substituting agents; in 1884 Berju (*Ber.*, **17**, 1403) obtained a dibromo-derivative of aminoazobenzene by the addition of bromine to an aqueous alcoholic solution of the base, but left its constitution undetermined; whilst Auwers states that when aminoazobenzene is nitrated in concentrated sulphuric acid solution, the nitro-group enters the aniline nucleus in the meta-position relatively to the amino-group, although acetylaminoazobenzene yields *p*-nitrobenzeneazoacetanilide under similar conditions (*Ber.*, 1900, **33**, 1314).

In order definitely to ascertain the action of bromine on aminoazobenzene, we carried out the reaction in glacial acetic acid solution in presence of fused sodium acetate, obtaining benzeneazo-*o*-*o*-dibromoaniline as sole product.

EXPERIMENTAL.

A solution of one part of aminoazobenzene and one and one-quarter parts of fused sodium acetate in ten parts of glacial acetic acid was cooled to 15°, and the thin paste gradually treated with two molecular proportions of bromine diluted with twice its weight of glacial acetic acid. A substance, green by reflected light, separated from the solution as the bromine was added, but after addition of three-quarters of the latter the colour began to turn brown. The separated product was collected by the aid of the pump, and after washing with dilute acetic acid and boiling with water formed a yellowish-brown powder which, in the crude condition, melted at 160—164°. The yield was about 80 per cent. of the theoretical. Beautiful golden-yellow needles melting at 168° (corr.) were obtained after two recrystallisations from boiling benzene:

0·1211 gave 0·1797 CO_2 and 0·0311 H_2O. C = 40·67; H = 2·85.

0·1904 ,, 0·2006 AgBr. Br = 44·84.

$C_{12}H_9N_3Br_2$ requires C = 40·56, H = 2·56, Br = 45·03 per cent.

The substance is readily soluble in warm acetone, hydrocarbons, or alcohols; the crimson solution in hot concentrated hydrochloric acid is so readily dissociated on addition of water as to render it extremely probable that the bromine atoms have entered the ortho-position relatively to the amino-group. A hydrochloride may be precipitated by passing dry hydrogen chloride into the benzene solution; it possesses a dark violet colour, resembling that of the corresponding salt of the unsubstituted compound, but on removal from the benzene immediately begins to turn yellow, even in a desiccator containing concentrated sulphuric acid.

Although Berju described his substance as melting at 152°, there is no doubt that he was working with the substance melting at 168°. A solution of one part of aminoazobenzene in ten parts of alcohol (96 per cent.) was treated with a solution of two molecular proportions of bromine in a mixture of three times its weight of water and six times its weight of alcohol. The precipitate was collected and washed with water until the wash-water was colourless; it then melted immediately at 154—156°, and after one crystallisation from benzene at 164·5—165·5°. A specimen which had been once recrystallised from benzene and once from alcohol melted at 167°, and when mixed with a specimen melting at 168°, prepared in acetic acid and sodium acetate solution, gave a melting point of 167·5—168°. Hence there is no doubt that the same substance is produced in both cases, although it is obtained in a purer form by the process we adopted.

The constitution of the dibromoaminoazobenzene was proved by its reduction to aniline and 2:6-dibromo-*p*-phenylenediamine. On account of the ease with which substances of this type lose bromine when reduced with tin and hydrochloric acid, sodium hyposulphite was employed. Two grams of sodium hyposulphite were added to one gram of the substance, suspended in 20 c.c. of alcohol and 10 c.c. of water. The mixture was boiled for half an hour, using a reflux condenser, alcohol being added at intervals. A colourless solution was obtained which, after being rendered strongly alkaline with sodium hydroxide, was freed from alcohol and aniline in a current of steam. A brown, crystalline substance remained, and was obtained in beautiful colourless needles melting at 137·5° after one recrystallisation from boiling water. Noelting, Grandmougin, and Michel (*Ber.*, 1892, **25**, 3334) give 138° as the melting point of 2:6-dibromo-*p*-phenylenediamine, whilst a specimen which we prepared by the reduction of 2:6-dibromo-4-nitroaniline melted at 137°, and a mixture of this with the substance just described melted at the latter temperature.

Diacetyl Derivative.—Dibromoaminoazobenzene, when boiled with acetic anhydride for two and a half hours, yields a *diacetyl* derivative melting at 137°. The substance is fairly soluble in warm ethyl acetate, and is deposited in beautiful yellow needles on cooling:

0·2339 gave 0·3779 CO_2 and 0·0672 H_2O. C = 44·06; H = 3·19.

$C_{16}H_{13}O_2N_3Br_2$ requires C = 43·74; H = 2·96 per cent.

Dibenzoyl Derivative.—The base was boiled with three times its weight of benzoyl chloride for thirty minutes, using a reflux condenser. The mass was poured into alcohol and boiled, the tarry substance thus being rendered crystalline. Very small, yellow needles melting at 220° were obtained on recrystallising the latter from boiling benzene:

0·1221 gave 0·2469 CO_2 and 0·0372 H_2O. C = 55·15; H = 3·39.
$C_{26}H_{17}O_2N_3Br_2$ requires C = 55·42, H = 3·02 per cent.

NOTE ON 2 : 6-DIBROMO-P-PHENYLENEDIAMINE.—This substance was originally prepared (*loc. cit.*) by the reduction of 2 : 6-dibromo-4-nitrophenylazoimide with tin and hydrochloric acid. As this involves the diazotisation of 2 : 6-dibromo-4-nitroaniline, an operation which is difficult to carry out, we decided to determine the conditions for the direct reduction of 2 : 6-dibromo-4-nitroaniline. One part of this base, three and a half parts of crystallised stannous chloride, and eight parts of concentrated hydrochloric acid were heated for three-quarters of an hour, using a reflux condenser. The clear liquid was decanted from any residue and cooled, when a tin double salt separated in considerable quantity, and a further portion was obtained by concentrating the mother liquors. The solution of the salt in hot water was freed from tin by hydrogen sulphide, filtered, and the base precipitated by ammonia. After recrystallisation from boiling water, colourless needles melting at 137° were obtained:

0·1380 gave 0·1960 AgBr. Br = 60·4.
$C_6H_6N_2Br_2$ requires Br = 60·2 per cent.

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CIX.—*The Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate.*

By FRANK TUTIN.

PERKIN and Prentice (Trans., 1891, **59**, 991) have described a synthesis of ethyl propanetetracarboxylate by the condensation of methylene chloride with the sodium derivative of ethyl malonate, and, as a by-product of the reaction, obtained a quantity of a yellow, crystalline substance which contained sodium.

Having had occasion to prepare ethyl propanetetracarboxylate, I employed the method described by Perkin and Prentice, and a quantity of the above-mentioned yellow by-product was isolated. After communicating with Prof. Perkin on the subject, this product was submitted to as complete an examination as was possible with the relatively small amount of material available. Two other crystalline by-products of the reaction were also investigated.

It has been found that the substances produced by the condensation of methylene chloride with the sodium derivative of ethyl malonate vary according to the conditions under which the reaction takes place. Six experiments were conducted, in three of which the mode of procedure was as follows. Ethyl malonate (64 grams) was added to a cold alcoholic solution of sodium ethoxide (9·2 grams Na in 200 c.c. of alcohol), after which the liquid became thick, owing to the separation of the sodium derivative of the ester. Methylene chloride (17 grams) was then added, thoroughly mixed, and the turbid liquid placed in four soda-water bottles and heated at 100° for two hours. At the end of this time the contents of the bottles no longer gave an alkaline reaction, but had a bright yellow colour and contained a quantity of a bulky solid. The alcohol was then removed by distillation, and, on fractionation, was found to contain about half the methylene chloride originally employed. Sufficient water was added to the pasty residue to dissolve the solid which it contained, and the esters were extracted from the resulting mixture by means of ether. During this operation a large quantity of the yellow sodium salt, observed by Perkin and Prentice, separated and was collected. The ethereal solution was washed with water until the aqueous liquid was no longer bright yellow, dried, and the ether removed. On fractionating the residual oil under 80 mm. pressure it was found that rather more than half of it consisted of unchanged ethyl malonate, the remainder being crude ethyl propanetetracarboxylate. The yield of the propane compound was never more than 20 per cent. of that theoretically possible, whereas that recorded by Perkin and Prentice was about 60 per cent. It may also be noted that on careful fractionation the boiling point of the ethyl propanetetracarboxylate was found to be 244°/80 mm., and not 234—236°/80 mm. as recorded by the previous investigators.

The aqueous liquid from which the esters had been separated by means of ether was acidified with sulphuric acid, when a quantity of a heavy oil was precipitated. After extracting this with ether, and completely removing the solvent, it slowly deposited a small amount of a crystalline *substance* which was removed by filtration. This substance dissolved readily in hot ethyl acetate, from which it separated in needles melting at 132°. On examining the oil which had been freed from the crystalline substance, it was found to contain some malonic acid, together with a small amount of the acid which yields the above-mentioned yellow sodium salt, but no other substance could be isolated from it.

Three other condensations were carried out in the manner already described, with the exception that the sodium was dissolved in only 150 c.c. of the alcohol, the other 50 c.c. being employed to dilute the malonic ester before mixing it with the sodium ethoxide. Working in this manner it was found that the sodium derivative of the ethyl malonate never separated, the liquid remaining quite clear. On heating this solution for two hours with methylene chloride it did not become so yellow, nor did it deposit so much solid as was the case in the experiments previously described, and it yielded none of the yellow sodium salt.* This was, moreover, not the only difference, for, although there was about the same yield of ethyl propanetetracarboxylate, considerably more unchanged ethyl malonate was recovered. Furthermore, the examination of the aqueous liquid from which the esters were separated yielded a different result. The heavy oil which was precipitated on acidifying the solution was extracted as in the previous experiments, but on standing, in addition to the compound melting at 132°, it deposited a *substance* which was insoluble in ethyl acetate.

As both unchanged ethyl malonate and methylene chloride were among the substances isolated from the reaction mixture, it appeared probable that the yield of ethyl propanetetracarboxylate might be increased if, at the end of two hours' heating, a further quantity of sodium ethoxide were added to the contents of the soda-water bottles, and the mixture again heated; this was found to be the case.

By employing methylene iodide in place of the chloride, and heating the mixture on a water-bath in a flask attached to a reflux condenser, Guthzeit and Dressel (*Annalen*, 1890, **256**, 171) obtained a yield of ethyl propanetetracarboxylate amounting to 84 per cent. of that theoretically possible. An experiment was therefore conducted with the use of methylene iodide, but the mixture was heated in soda-water bottles at 100°. Under these conditions it was found that the product consisted entirely of about equal proportions of ethyl malonate and ethyl methylenemalonate, no ethyl propanetetracarboxylate being obtained.

Examination of the Yellow Sodium Salt.

The yellow sodium salt, which was obtained in glistening leaflets, was purified by recrystallisation from alcohol:

0·1288 gave 0·0191 Na_2CO_3. Na = 6·4.

$C_{14}H_{21}O_6 \cdot CO_2Na$ requires Na = 6·5 per cent.

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* In one experiment, where the heating had been prolonged to three hours, a very small amount of this salt was obtained.

On treatment with sulphuric acid this salt yielded a liquid *acid* which gave a deep violet coloration with ferric chloride:

0·1314 gave 0·2630 CO_2 and 0·0798 H_2O. C = 54·6; H = 6·7.
0·1304 ,, 0·2607 CO_2 ,, 0·0786 H_2O. C = 54·5; H = 6·7.
$C_{15}H_{22}O_8$ requires C = 54·5; H = 6·6 per cent.

0·2148 neutralised 6·7 c.c. *N*/10 NaOH.
$C_{14}H_{21}O_6{\cdot}CO_2H$ requires 6·5 c.c.

A molecular weight determination by the cryoscopic method gave the following result:

0·3160 dissolved in 33 of phenol gave Δ^t - 0·220°. M.W. = 331.
$C_{15}H_{22}O_8$ requires M.W. = 330.

From these results it appears that the yellow by-product is the sodium salt of an acid possessing the formula $C_{14}H_{21}O_6{\cdot}CO_2H$.

Hydrolysis of the Acid $C_{14}H_{21}O_6{\cdot}CO_2H$.—A quantity of the yellow sodium salt was boiled with a large excess of an aqueous solution of potassium hydroxide. During the first half-hour the yellow colour of the liquid became deeper, and it was found that if the hydrolysis was stopped at the end of this time, the liquid acidified and extracted with ether, an *acid* melting at 305° was obtained. When, however, the heating was continued for five hours, the solution became colourless, and, on acidifying and extracting with ether, it then yielded an *acid* which, when crystallised from ethyl acetate, melted at 138—139°:

0·1053 gave 0·1782 CO_2 and 0·0447 H_2O. C = 46·1; H = 4·7.
0·0987 ,, 0·1662 CO_2 ,, 0·0418 H_2O. C = 45·9; H = 4·7.
$C_{10}H_{12}O_8$ requires C = 46·1; H = 4·6 per cent.

0·1172 neutralised 18·3 c.c. *N*/10 NaOH.
$C_6H_8(CO_2H)_4$ requires 18·1 c.c.

The acid melting at 138—139°, therefore, possesses the formula $C_6H_8(CO_2H)_4$. It is a saturated compound, and must therefore contain in its structure a closed ring. Although it melts at the same temperature as *cis-cyclo*hexane-1 : 2 : 4 : 5-tetracarboxylic acid (Gregory and Perkin, Trans., 1903, **83**, 787), the two compounds are not identical, as the *barium* and *calcium* salts of the acid here described are readily soluble in water, the latter salt crystallising in needles from dilute alcohol. Moreover, the acid obtained by the hydrolysis of the yellow sodium salt does not yield a dianilic acid similar to that prepared from the *cyclo*hexane acid, but gives a *compound* (m. p. 224°) which is insoluble in aqueous alkalis.

The formation of a tetracarboxylic acid, $C_{10}H_{12}O_8$, by the hydrolysis of a monocarboxylic acid possessing the formula $C_{15}H_{22}O_8$, would seem to indicate that the latter compound was the diethyl mono-methyl ester of the former, but it is difficult to see how this can be the case. Moreover, a compound that was simply a tri-ester of a tetracarboxylic acid would not be expected to yield a coloured sodium salt or to give a violet coloration with ferric chloride. These considerations, together with the fact that the tetracarboxylic acid is not the first product of the hydrolysis of the yellow sodium salt, but is only produced by prolonged action of the alkali, lead to the conclusion that the acid, $C_6H_8(CO_2H)_4$, is not formed by simple hydrolysis of the acid $C_{14}H_{21}O_6{\cdot}CO_2H$, but is the product of some more profound change.

Examination of the Substance Melting at 132°.

The substance melting at 132°, obtained as previously described, crystallises from a mixture of alcohol and ethyl acetate in flattened needles. It is very slightly volatile in steam, and gives a deep wine-red colour with ferric chloride:

0·0985 gave 0·2034 CO_2 and 0·0557 H_2O. $C = 56·3$; $H = 6·3$.
0·1004 ,, 0·2074 CO_2 ,, 0·0576 H_2O. $C = 56·3$; $H = 6·3$.
$C_{20}H_{26}O_{10}$ requires $C = 56·3$; $H = 6·1$ per cent.
0·1000 neutralised 4·3 c.c. *N*/10 NaOH.
$C_{18}H_{24}O_6(CO_2H)_2$ requires 4·6 c.c.

When hydrolysed with potassium hydroxide, this compound gave an *acid* which crystallised from alcohol in plates melting at 306°, gas being suddenly evolved.

Examination of the Substance Insoluble in Ethyl Acetate.

This product consisted of minute, slightly yellow needles, which were insoluble, or nearly so, in all solvents. When heated it assumed a deep orange colour, and decomposed above 295°. It was heated with a dilute solution of sodium carbonate, when it was gradually hydrolysed and dissolved. On cooling the solution, a *sodium* salt separated in white needles:

0·1600 of salt crystallised from water, on heating at 125°, lost 0·0182 H_2O. $H_2O = 11·4$.
0·1418 of anhydrous salt gave 0·0369 Na_2SO_4. $Na = 8·4$.
0·0905 ,, ,, 0·0175 Na_2CO_3. $Na = 8·4$.
$C_{32}H_{35}O_{20}Na_3,6H_2O$ requires $H_2O = 11·7$ per cent.
$C_{32}H_{35}O_{20}Na_3$ requires $Na = 8·5$ per cent.

The corresponding *potassium* salt is insoluble in water and is anhydrous; it can be crystallised from glacial acetic acid:

0·1049 gave 0·0325 K_2SO_4. $K = 13·8$.
$C_{32}H_{35}O_{20}K_3$ requires $K = 13·7$ per cent.

The acid was prepared in the following manner. The salt was dissolved in warm concentrated hydrochloric acid, water then immediately added, and the precipitated *acid* collected on a filter. These operations must be conducted as rapidly as possible, as the organic acid is readily acted on by the mineral acid. The acid prepared in this way crystallises from ethyl acetate in leaflets melting at 200°, and gives an intense reddish-brown coloration with ferric chloride:

0·1117 gave 0·2132 CO_2 and 0·0526 H_2O. C = 51·8; H = 5·2.
0·1096 „ 0·2084 CO_2 „ 0·0527 H_2O. C = 51·8; H = 5·3.
$C_{32}H_{38}O_{20}$ requires C = 51·8; H = 5·1 per cent.

The author desires to express his thanks to Mr. A. C. O. Hann for assistance rendered in connexion with this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CX.—*The Chemical Composition of Petroleum from Borneo.*

By HUMPHREY OWEN JONES and HUBERT ARTHUR WOOTTON.

THE mineral oil found in such large quantities in the Koetei district in Borneo differs in a very striking way from all other oils which have been examined hitherto, and a brief account of the results obtained in an examination of the chemical composition of these oils forms the subject of this communication.

The oils which we examined some eighteen months ago were obtained through Messrs. M. Samuel and Co.

The crude oils are of a brown colour, with densities varying from 0·83 to 0·87 at 15°, and may be divided roughly into two classes. The first class, which is obtained from a larger number of wells than the other, consists of oils which leave a residue of paraffin wax after distillation. The second class consists of oils which leave no wax, but a viscous residue described as "asphalte." There is no essential difference between the more volatile fractions of these two classes of oils.

On distilling the crude oil, liquid does not pass over until the oil has reached a temperature of about 100°. The distillate is quite colourless until about 260° is reached; but all the distillates above 180° acquire a yellow colour on exposure to the air. The portions of highest boiling point very rapidly become reddish-yellow.

The specific gravities of all the distillates are higher than those of the corresponding distillates of American and Russian oils, as may be seen from the data appended, which refer to a sample of crude oil sp. gr. = 0·845 distilled from an ordinary flask.

Boiling point.	Percentage by volume.	Sp. gr. at 15°.
100—140°	15·4	0·758
140—180	22·0	0·812
180—220	9·4	0·827
220—260	9·5	0·846
260—300	19·0	0·880
Residue above 300°	24·5	solid

The distillates were fractionated repeatedly, using a twelve-pear column, and also using large fractionating columns filled with beads and surmounted by a constant-temperature still-head.

The most volatile fractions boiling between 35° and 60° were present in very small quantities, and from their specific gravities and general behaviour were found to consist chiefly of saturated paraffins.

The fractions boiling above 60° possessed specific gravities greater than those of the polymethylene compounds and approximating to those of the olefines; but they did not react readily with bromine, and when they did so hydrogen bromide was evolved.

The fraction boiling at 80—83° had a specific gravity of 0·866 at 15°, which is very close to that of benzene (0·874). This fraction also possessed the odour of benzene. The various fractions were therefore treated with a mixture of nitric and sulphuric acids, and were found to yield nitro-derivatives of aromatic hydrocarbons, even when the temperature was kept at 0°. The nitration mixture separates into three layers, the lowest layer consisting of sulphuric acid with some nitric acid; the middle layer is a yellow oil consisting of nitro-compounds with some unnitrated oil and some acid in solution, and the top layer is a colourless oil consisting of substances which do not further react with the nitric-sulphuric acid mixture and some nitro-compounds in solution.

The oil was shaken with the mixture of nitric and sulphuric acids until no further action took place. The two upper layers were then separated from the acids, washed repeatedly with water and sodium carbonate solution, dried and distilled.

The first portion of the distillate consisted of a colourless, mobile oil boiling at about the same temperature as the fraction taken for nitration; then the temperature rose rapidly about 120° and the yellow nitro-compound distilled over.

The nitro-compounds obtained from the lower fractions were identified by conversion into amines by reduction and then converting the amines into acyl derivatives or salts.

In this way it was shown that the oil contained benzene, toluene, *m*-xylene and mesitylene. Other aromatic hydrocarbons were present in these and in the less volatile fractions, but they were not separated.

Benzene was found among the distillates boiling between 55° and 83°, as it forms mixtures of constant boiling point with hexane and with *cyclo*hexane, both of which were present.

The portion of the oil not acted on by the mixture of nitric and sulphuric acids was further fractionated and found to consist of a mixture of saturated paraffins and of hydrocarbons of the *cyclo*hexane series in approximately equal quantities. A complete separation, however, was not effected.

The methods adopted for the identification of the hydrocarbons consisted in determinations of (1) boiling point, (2) density of the liquid, (3) vapour density (Hofmann's method), (4) carbon and hydrogen contents, and in an examination of chemical properties such as reaction with bromine or with a nitric-sulphuric acid mixture (not at 0°).

The percentage of aromatic hydrocarbons found varied from 25 to 40.

Aromatic hydrocarbons exist in other oils, but only in much smaller quantities, almost insignificant in many cases, being at the most about 2 per cent.

The oil is free from sulphur, and gives no indophenine reaction. Hence, when nitrobenzene derived from it is converted into aniline, the latter keeps its colour without perceptible change for long periods of time when exposed to light and air.

Basic and acidic constituents, except in minute traces, are absent from the oil.

It was mentioned above that the less volatile portions of the oil rapidly acquired a yellow colour on exposure to air. This is due to oxidation, since there is no coloration produced when the oil is kept in hermetically sealed glass vessels.

The compounds which undergo oxidation are partly removed by treatment with sulphuric acid.

In an attempt to isolate some of these compounds the oil was treated with picric acid; this dissolves readily in the oil, forming a deep red solution, which on standing deposits reddish-orange prismatic crystals melting at some temperature between 105 and 114°. The melting point of the picrate was almost independent of the boiling point of the fraction of oil from which it was obtained; but the fractions boiling below 180° gave no picrate, and those boiling below 210° gave very little. The weight of picrate obtainable from a litre of oil boiling between 150° and 280° is about 129 grams.

The picrate was distilled in steam and was found to decompose slowly into picric acid and a yellowish oil, which distilled with the steam, and was collected, dried and fractionated.

The oil was found to consist of the members of the naphthalene series, among which naphthalene, α- and β-methylnaphthalenes and a dimethylnaphthalene were recognised. Higher homologues were also present.

In the flask after continued distillation there were still left some dark red needles, which were separated mechanically from picric acid and recrystallised from dilute alcohol several times, when they melted sharply at 122—123°. Analysis gave:

$C=56{\cdot}5$; $H=3{\cdot}8$; $N=11{\cdot}2$ and $11{\cdot}3$.

$C_{12}H_{12},C_6H_2(NO_2)_3{\cdot}OH$ requires $C=56{\cdot}2$; $H=3{\cdot}9$; $N=10{\cdot}9$ per cent.

The hydrocarbon was obtained by steam distillation from alkaline solution, dried and distilled. It was found to be a pale yellow oil burning at 265 = 266°. Analysis gave:

$C=92{\cdot}0$; $H=7{\cdot}7$; V.D. $(H=1)=77$.

$C_{12}H_{12}$ requires $C=92{\cdot}3$; $H=7{\cdot}7$ per cent.; V.D. $=78$.

The hydrocarbon was therefore β-dimethylnaphthalene, and differed from the other dimethylnaphthalene mentioned above.

The quantity of naphthalene hydrocarbons existing in the petroleum was about 6—7 per cent.

The solid wax found in the residues after distillation was distilled in a vacuum, and was obtained as a colourless substance, crystallising in plates with a pearly lustre, melting about 55°. and having all the characteristics of the higher members of the paraffin series.

It is very interesting to notice that the less volatile portions of Borneo petroleum are optically active, which fact shows that this oil, like the others, is probably of organic origin.

The rotations observed were within the limits, 0·07° to 0·7° in a 2-dcm. tube, observed by Rakusin for American and Russian oils (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 554).

The whole fraction boiling at 260—340° gave α_D $-0{\cdot}18$ in a 2-dcm. tube. American and Russian oils are usually dextrorotatory.

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CAMBRIDGE.

CXI.—*The Relation between the Crystalline Form and the Chemical Constitution of Simple Inorganic Substances.*

By WILLIAM BARLOW and WILLIAM JACKSON POPE.

IN a previous paper we have shown that the main aspects of the doctrine of valency appear as the expression of certain well-defined geometrical properties of arrangements in space if a very simple conception is adopted as to the nature of crystalline substances (Trans., 1906, **89**, 1675). It has also been shown that the crystalline forms of a large number of chemical substances are derivable from their compositions and constitutions on the basis of this conception. Briefly stated, the concept adopted is that in a crystalline substance the spheres of influence of the component atoms are homogeneously arranged to form a close-packed assemblage; a molecule is therefore a closely arranged group consisting of certain of the spheres of atomic influence. These spheres or domains are conceived to fill space, and are therefore not strictly spherical in form, but are polyhedra enclosed by interfaces drawn at right angles to lines joining adjacent centres of atomic influence. For the purpose of graphically picturing the conditions prevailing in assemblages of atoms, represented by their respective spheres of influence, the mechanical expedient is adopted of squeezing together masses of solid indiarubber balls of appropriate sizes and suitable arrangement so that the interstices become practically eliminated by the interaction of the balls. The balls then exercise mutual repulsions of the nature previously postulated (*loc. cit.*, 1676), and it is suggested that the equilibrium arrangement reached by this conversion of deformable, but incompressible, spheres into space-filling polyhedra accurately represents the allotment among the atoms of a chemical substance of the space which it occupies. Inasmuch as for purposes of demonstration the packing of hard undeformable spheres can be more readily depicted than that of those just described, it is convenient to employ the former in place of the latter, and to apply the term sphere of atomic influence, although the atomic domain is actually polyhedral in shape. The correspondence between the conditions of equilibrium of a close-packed assemblage of hard spheres and of a close-packed assemblage of elastic and deformable, but incompressible, spheres is discussed in connexion with the simplest types of equilibrium assemblages (p. 1157).

In the paper referred to it is shown by numerous instances that homogeneous, close-packed assemblages of spheres, from which the interstices have been eliminated in the manner described, are characterised by the possession of three geometrical properties, two of which may be here again noted.

If from such an assemblage, one homogeneously situated set of spheres, each sphere having the volume m, is removed, the vacated spaces can be re-occupied each by several spheres having the total volume m, in such a manner that the close-packing may be restored by mere distortion and local adjustment without remarshalling the assemblage. This, the first geometrical property of close-packed homogeneous assemblages, is discussed in more detail on p. 1204; it corresponds entirely with that aspect of valency which states that an atom of valency m is replaceable in a compound by several atoms of the total valency m.

Again, if in such an assemblage, one homogeneously situated set of spheres, each of volume m, is homogeneously replaced by a set of spheres, each of volume $m+1$, or if to each of the original spheres of volume m is added one of volume 1 in similar contact with it, the assemblage being homogeneously opened or spread out for the purpose, it is found that, if remarshalling does not take place, close-packing can only be restored by the insertion into gaps produced in the assemblage of additional spheres in the proportion of volume 1 for each original volume m concerned. The replacement of a sphere of volume m by others of the total volume $m+1$ thus necessitates the simultaneous addition of another sphere of volume 1; in other words, an atom of valency m may be replaced by others of total valency $m+2$, $m+4$, &c. This, the second geometrical property, corresponds exactly with the known facts that when an element changes its valency it in general does so by two, or multiples of two, units or minimum valency volumes, and also that a substitution like that of N by C, as in $CH_3{\cdot}NH_2$, necessitates the addition of another univalent atom to the added carbon atom, so as to give $CH_3{\cdot}CH_3$ in the quoted instance. Many quantitative data were adduced bearing on the applications of the first and second geometrical properties for the purpose of showing that the fundamental valency of an atom is approximately proportional to the volume appropriated by the polyhedron representing it in the crystal structure. It was thus proved that the diagrammatic method of representing molecular constitution which we introduced, and according to which each atom present in a given compound is represented by a sphere of influence approximately proportional in volume to its fundamental valency, is entirely in harmony with accepted chemical theory.

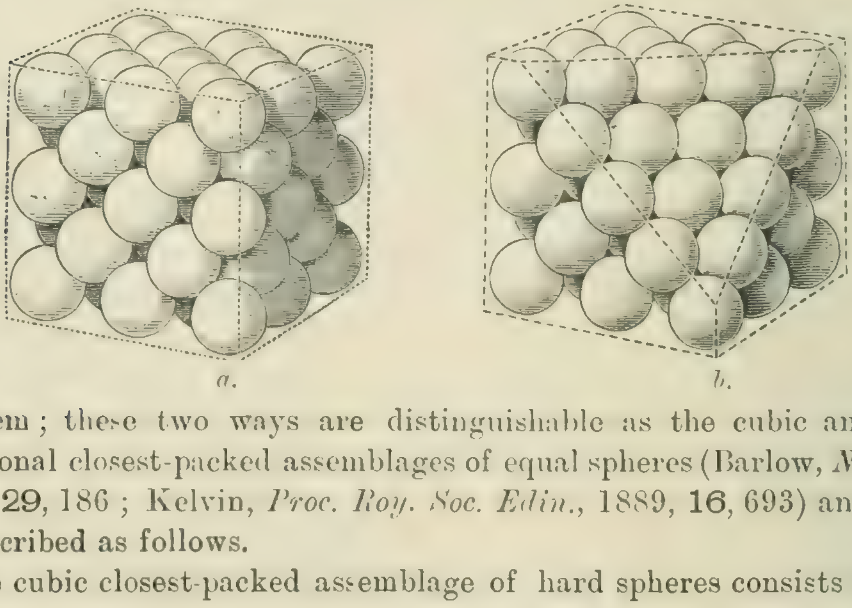
The fact that the methods in question were found to represent adequately the constitutions and inter-relations of a number of aromatic compounds, endows the Frankland doctrine of valency with a real physical signification; the classificatory scheme based on the doctrine of valency and the theory of constitutional formulæ thus acquires a more graphic expression and also a justification. It is, however, desirable that the new method of investigation should be applied to a number of complete classes of simple chemical substances, because by so doing a demonstration of the truth of our former conclusions can be given which is practically independent of the previous one. We proceed to deal in the first place with practically all those substances composed of atoms of the same fundamental valency which have been sufficiently completely examined goniometrically for our purpose; these substances include the elements, most binary compounds, and compounds of the type of the salts KI_3, KI_5, and K_2AgI_3. Some corresponding ammonium salts are also considered.

The validity of the conclusion that the spheres of influence of atoms of the same fundamental valency occurring in the same compound are nearly of the same size is severely tested by the limitation which this imposes on the constitution of the assemblage; the limitation in question is expressed as a fourth geometrical property of close-packed assemblages in the following pages.

The Closest-packed Homogeneous Assemblages of Equal Spheres.

If all the atoms composing a crystalline structure are identical in kind and in environment and are without polarity, the structure may be simulated by a homogeneous, closest-packed assemblage of equal spheres. Equal, deformable, incompressible spheres can, like hard spheres, be closest-packed under a general pressure so as to form a homogeneous structure in two, and only two, ways, or in a homogeneous combination of them; these two ways are distinguishable as the cubic and the hexagonal closest-packed assemblages of equal spheres (Barlow, *Nature*, 1883, **29**, 186; Kelvin, *Proc. Roy. Soc. Edin.*, 1889, **16**, 693) and may be described as follows.

FIG. 1.



a. *b.*

The cubic closest-packed assemblage of hard spheres consists of an arrangement of equal spheres in contact as depicted in Figs. 1, *a* and *b*, and exhibits the following as its principal elements of symmetry. It possesses three sets of planes of symmetry—the cube planes—parallel to the planes of a cubic partitioning of space; it contains three sets of axes (axial directions) of four-fold symmetry perpendicular to those planes and four sets of axes of three-fold symmetry symmetrically inclined towards the three intersecting cube planes of symmetry. The axes of three-fold symmetry are perpendicular to the planes of closest-packing of spheres in the system; there are four non-parallel planes of section of this latter kind and they lie parallel to the faces of the regular octahedron obtained by symmetrically cutting off the cube corners. A projection of the system on one of these planes of section is shown in Fig. 2. Six sets of planes of symmetry bisect the solid angle between any two cube planes of symmetry; these planes are parallel to the dodecahedron planes of the form $\{110\}$ and the projection of the structure upon them is shown in Fig. 3. Six sets of axes of two-fold symmetry lie perpendicular to the dodecahedron planes. The sphere-centres, the sphere contacts and the middle points of octahedral groups of the spheres are all centres of symmetry. The assemblage can be regarded as composed of layers having the square arrangement depicted in Fig. 4, in which sections through consecutive layers are represented by continuous and dotted circles, or as composed of the triangularly

FIG. 2.

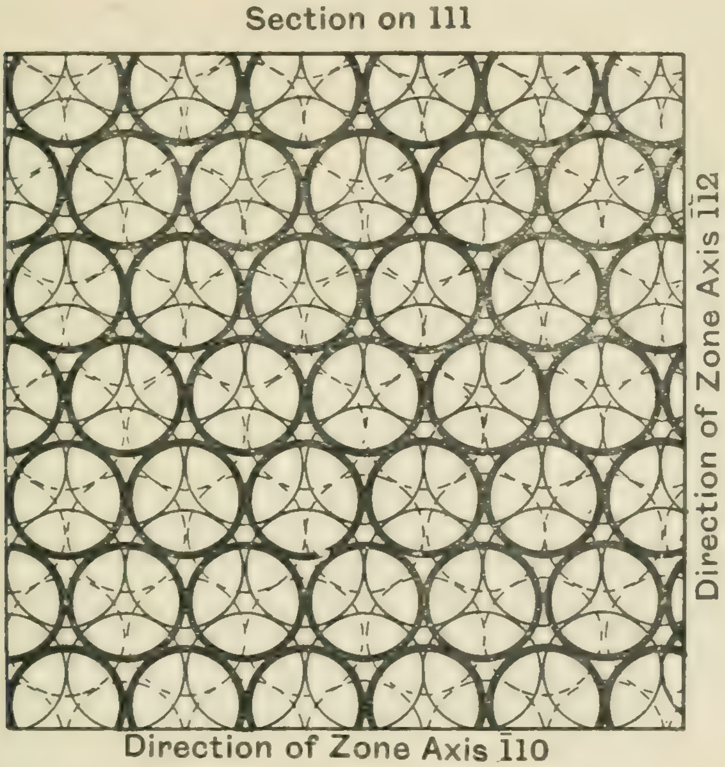

Section on 111
Direction of Zone Axis $\bar{1}\bar{1}2$
Direction of Zone Axis $\bar{1}10$

FIG. 3.

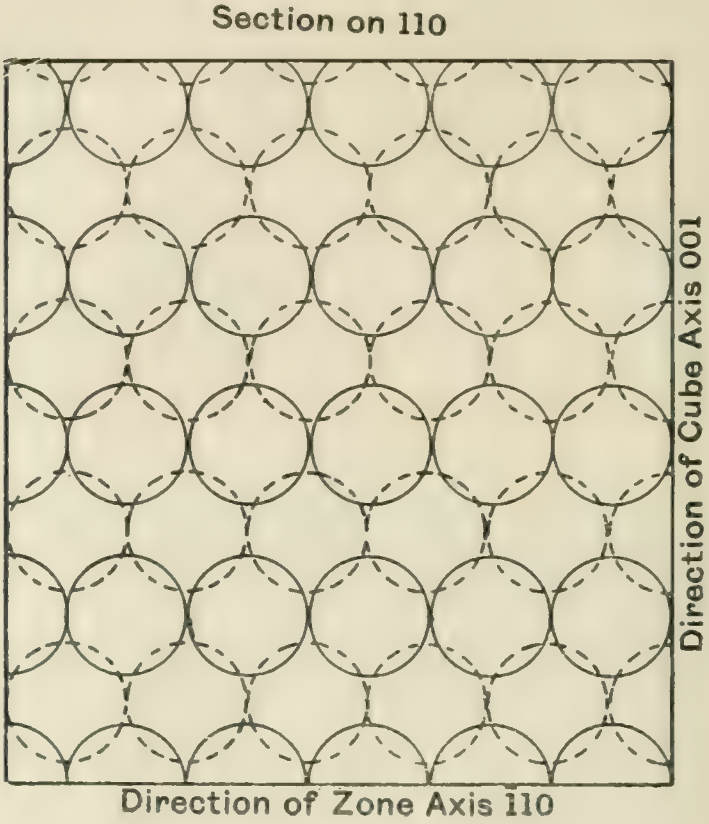
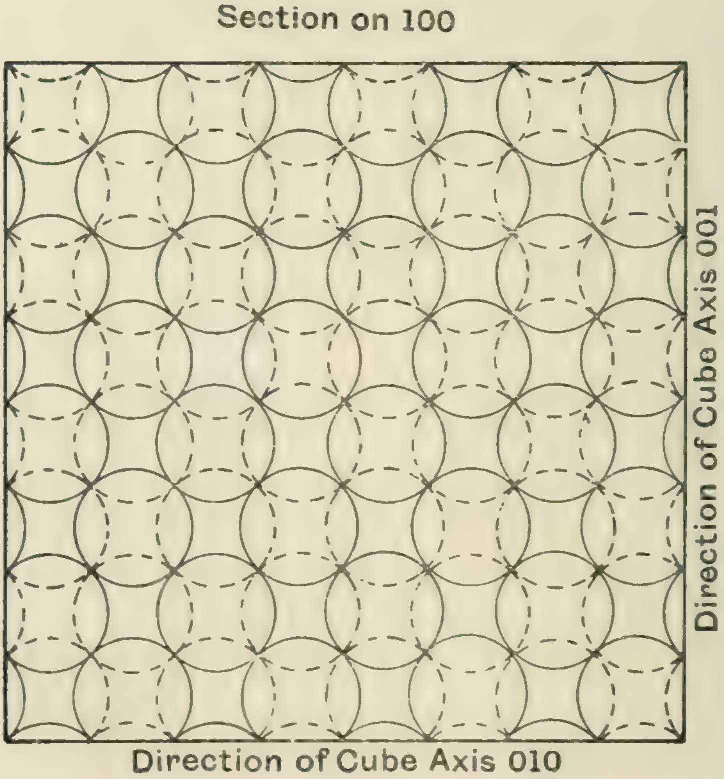

Section on 110
Direction of Cube Axis 001
Direction of Zone Axis 110

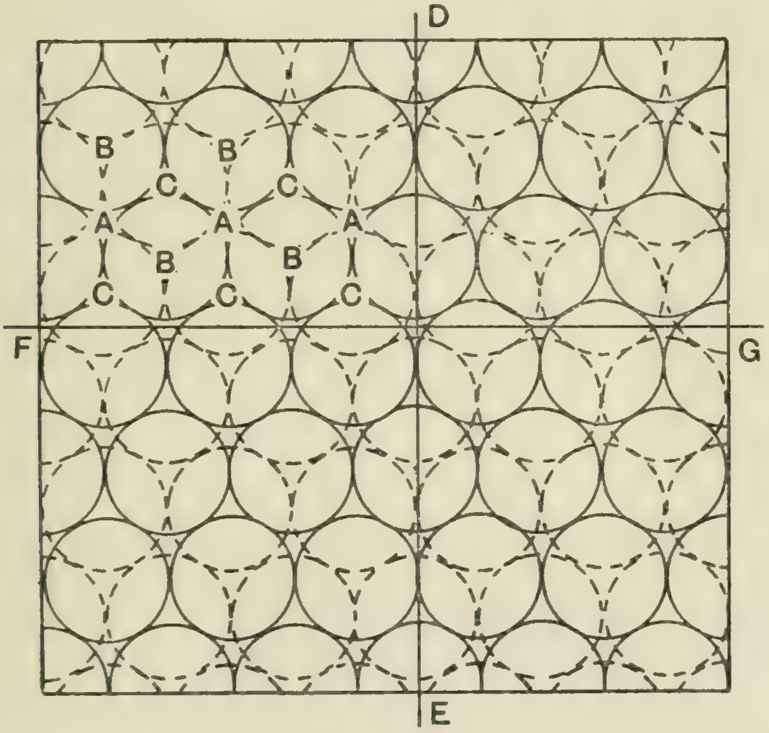
FIG. 4.


Section on 100
Direction of Cube Axis 001
Direction of Cube Axis 010

arranged layers projected in Fig. 2; in the former case, alternate layers have the same projection on a plane parallel to a cube face, whilst in the latter, three consecutive layers, indicated by different kinds of lines in Fig. 2, have different projections on the octahedron plane, the projections of the first, fourth, and seventh, those of the second, fifth, and eighth, those of the third, sixth, and ninth, &c., being respectively identical. This closest-packed arrangement of equal spheres is well known to chemical engineers (see Rauter, *Betriebsmittel der chemischen Technik*, 1905, 456); it possesses the symmetry of the holohedral cubic crystalline system.

The hexagonal closest-packed assemblage also consists of an arrangement of equal spheres in contact, but its alternate closest-packed layers have the same projection on the plane of a layer as shown in Fig. 5.

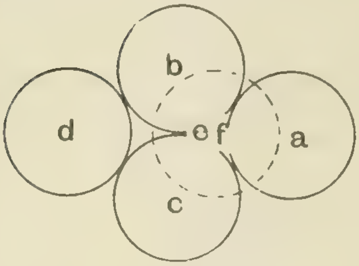
FIG. 5.



It possesses the following elements of symmetry. Planes of symmetry intersect the sphere centres of each of its closest-packed triangularly arranged layers. Screw axes of six-fold symmetry pass, perpendicular to these planes, through the centres of the strings of cavities and do not intersect any of the spheres; they are projected at points of the kind *A* in the diagram. Rotation axes of three-fold symmetry also pass perpendicularly through the layers; they are projected at points of the kinds *B* and *C*. Three sets of planes of symmetry occur which contain the six-fold screw axes and pass through nearest sphere centres of consecutive layers; the projection of one of these is marked *DE* in

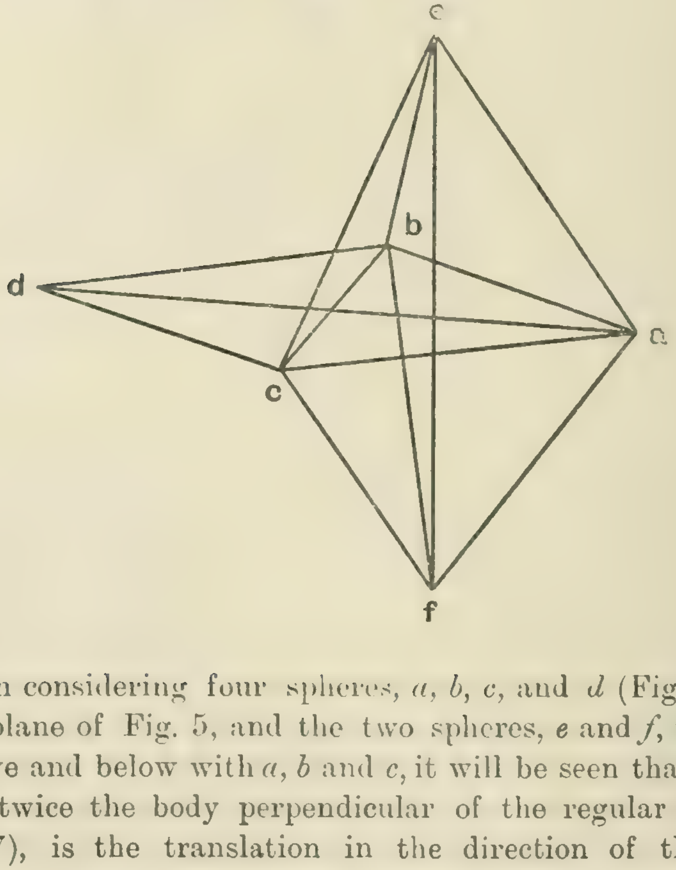
Fig. 5. Three double sets of digonal axes lie perpendicular to the last described planes of symmetry and intersect the six-fold screw axes; these digonal axes lie in planes midway between the layers of centres referred to. There are three sets of planes of gliding symmetry containing nearest six-fold screw axes and a projection of one of these is marked *FG*; three double sets of digonal axes lie perpendicular to these latter planes in the planes containing the sphere centres. Finally, centres of symmetry are found in planes midway between the layers of centres both on the six-fold screw axes and at points midway between them. The assemblage displays holohedral hexagonal crystalline symmetry.

FIG. 6.



The symmetry of cubic closest-packed assemblages is so high that the relations between all their dimensions are defined by the symmetry; this, however, is not the case in the hexagonal closest-packed assemblage of equal spheres, and the axial ratio, $a:c$, for the structure has therefore to be calculated from the translations of the system of

FIG. 7.

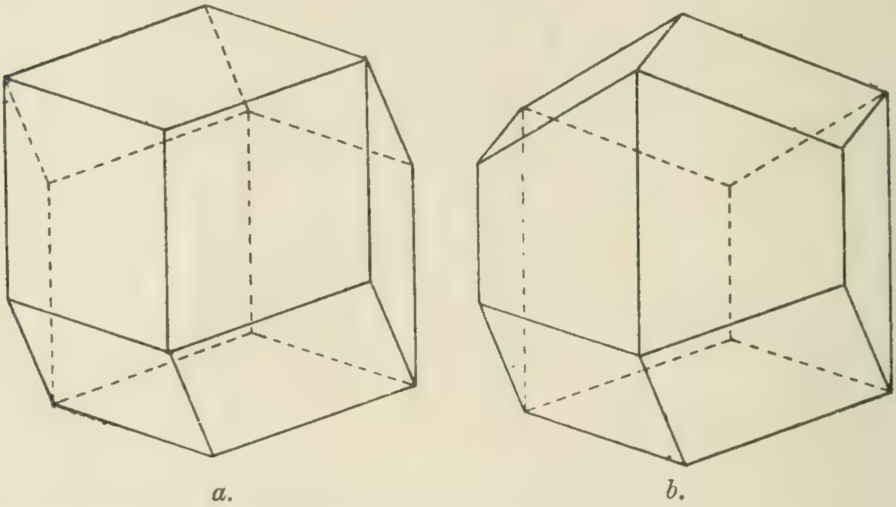


spheres. On considering four spheres, *a*, *b*, *c*, and *d* (Fig. 6), in contact in the plane of Fig. 5, and the two spheres, *e* and *f*, which make contact above and below with *a*, *b* and *c*, it will be seen that the length, *ef*, namely, twice the body perpendicular of the regular tetrahedron *abce* (Fig. 7), is the translation in the direction of the principal axis, whilst in the plane perpendicular to the principal axis two translations occur, namely, one equal to the side, *ac*, of a regular tetrahedron and the other equal to *ad*, which is double the face perpendicular of the tetrahedron. Taking the side of a regular tetrahedron as 1, the face perpendicular is $\frac{1}{2}\sqrt{3}$ and the body perpendicular is $\sqrt{\frac{2}{3}}$. The symmetry demands that the crystallographic axis c shall be chosen in the direction of the principal axis of symmetry in which the translation is *ef*, but leaves the usual choice for the direction of the axis a as that of either the translation *ab* or *ad*. Selecting the directions of *ab* and *ef*, for those of the axes a and c respectively, the axial ratios must be values compatible with $a:c = ab:ef = 1:2\sqrt{\frac{2}{3}} = 1:1{\cdot}6330$, and this value or one-half thereof, $a:c = 1:0{\cdot}8165$, may be expected to recur as descriptive of closest-packed hexagonal assemblages. The translations *ad* and *ef* cannot, however, be at once compared for the purpose of calculating simple axial ratios for the assemblage; it will be seen that if the directions of *ad* and *ef* are chosen as axial directions, the co-ordinates must be taken as $ef/2$ and $ad/3$, these lengths representing the points at which the two lines cut each other. The ratio, $a:c = 2/3\ ad:ef = \frac{2}{3}\sqrt{3}:2\sqrt{\frac{2}{3}} = 1:\sqrt{2} = 1:1{\cdot}4142$, is therefore an alternative expression for the hexagonal closest-packed assemblage equally appropriate with the ratio $a:c = 1:1{\cdot}6330$. The relation between these values of the axial ratio is the customary one of the kind, $1{\cdot}4142 = 1{\cdot}6330 \times 0{\cdot}866$, the factor 0·866 expressing the ordinary relation between the two alternative sets of axial ratios available for all trigonal or hexagonal crystalline substances.

When the elastic deformable spheres are employed instead of the hard spheres in the formation of the closest-packed assemblages just described, and an equable pressure is applied in all directions to the assemblage, it is clear that the relative arrangement of the sphere-centres survives the compression; each sphere is similarly flattened, becoming converted into a twelve-faced plane-sided figure, and the plane faces bisect at right angles lines joining nearest sphere centres. Fig. 8, *a* and *b*, shows the forms of the polyhedra thus produced from each sphere in the cubic and the hexagonal assemblage respectively; the packing together of a number of either kind of polyhedra fills space without leaving interstices.

It is convenient in this connexion to direct attention to the corresponding properties which inter-relate assemblages of hard and of deformable spheres. In the case of the former, closest-packing stands for stable equilibrium, and in the latter, stable equilibrium implies the most equable possible distribution of the pressures. As the degree of pressure at a place of contact between two spheres is measurable by the amount of mutual deformation which their interaction produces, an arrangement which gives a maximum number of contacts in an assemblage of hard spheres, and consequently a minimum amount of interstitial space, has its complete counterpart, so far as arrangement is concerned, in an assemblage similarly composed of deformable spheres; for in the latter the maximum number of contacts will have become a maximum number of places of equal pressure and deformation. When, therefore, for sake of convenience, hard spheres are employed, it must not be supposed that some condition is imported which is not represented in an appropriate arrangement of those polyhedra into which deformable spheres have been converted by an equable pressure; the latter kind of assemblage is, in all cases, to be regarded as the one actually employed to depict the conditions, and any property of an assemblage of hard spheres which is not paralleled in the corresponding assemblage of polyhedra should be regarded as irrelevant.

FIG. 8.



The two assemblages above described are equally close packed and can, by combination or admixture, give rise to other equally close-packed homogeneous assemblages; there are no other methods of obtaining closest-packed homogeneous assemblages of equal spheres, although other homogeneous assemblages of equal spheres can be built up which are nearly as close-packed as these.

The Crystalline Forms of the Elements.

It has long been known (Groth, *Die Molekularbeschaffenheit der Krystalle*, 1888) that the elements, in general, crystallise in either the cubic or the hexagonal system, although some striking exceptions to this rule occur. Retgers (*Zeitsch. physikal. Chem.*, 1894, **14**, 1), who studied this question in detail, showed statistically that the greater the number of atoms present in the molecule of a given compound the less is the likelihood of its crystallising in one of the systems of high symmetry; table I gives a summary of his data and states the percentage number of crystallographically examined substances of different degrees of molecular complexity which crystallise in the various crystalline systems.

TABLE I.

		Inorganic substances, the number of atoms in molecule of which is respectively:					
System.	Elements.	2.	3.	4.	5.	more than 5.	Organic substances.
Cubic	50	68·5	42	5	12	5·8	2·5
Hexagonal	35	19·5	11	35	38	14·6	4·0
Tetragonal	5	4·5	19	5	6	7	5·0
Orthorhombic	5	3·0	23·5	50	36	27·3	34·0
Monosymmetric	5	4·5	3	5	6	37·3	47·5
Anorthic	0	0	1·5	0	2	8	7·0
Number of cases examined for each vertical column	40	67	63	20	50	673	585

The fact that some 85 per cent. of the elements crystallise in either the cubic or the hexagonal system will naturally be considered in connexion with the geometrical fact that the two closest-packed homogeneous assemblages of equal spheres respectively possess cubic or hexagonal symmetry. The existence of holohedral cubic or hexagonal symmetry, with the crystallographic dimensions indicated above, requires that any grouping which exists shall be in harmony with the symmetry; if, therefore, molecular complexes are agglomerated in a manner which is not compatible with the elements of symmetry of either of the above-mentioned kinds of closest-packing, some form of symmetry other than either the holohedral cubic or hexagonal one described must be looked for. It is easy to conceive types of molecular aggregation which would thus fail to conform to the high symmetry concerned, and when the general pressure which eliminates the interstitial space is exerted upon these less symmetrical forms, the resulting assemblage will not precisely simulate either the closest-packed cubic or hexagonal assemblage of equal deformable spheres. Other causes leading to a slight departure from the described assemblages may be suggested, such, for instance, as a minute polarity of the constituent spheres, but the available data are not sufficient to allow of the causes being precisely traced. It is, however, important to notice that the departures from the precise forms indicated, and which have to be accounted for, are mechanically producible by a very simple expedient. They can, in fact, be exactly imitated by forming and compressing a cubic or a hexagonal closest-packed assemblage in which certain of the spheres, arranged homogeneously, differ very slightly in size from the others; this naturally corresponds to the assumption that during the process of molecular aggregation, either preliminary to, or synchronous with, crystallisation, certain constituent atoms obtain by some means or other slightly different treatment as compared with the others in the resulting structure. As will be indicated, this difference is minute in amount, but its effect can be distinctly followed in the crystallographic measurements.

It is thus necessary to trace the effect of making some of the spheres in various assemblages differ slightly in size from others, and before proceeding to the discussion of individual cases it is desirable to indicate another geometrical property of close-packed assemblages; this is conveniently described as the fourth of such properties.

If nearly equal deformable and incompressible spheres, of a limited number of sizes, are close-packed under a general pressure in such a way as to form a homogeneous assemblage, their marshalling will in many cases closely approximate to that which characterises one of the two closest-packed assemblages of equal spheres. This fourth geometrical property acquires importance in connexion with the crystalline form of the elements as well as in cases of compounds composed of elements of equal valency.

The elements Cu, Ag, Au, C, Si, Pb, As, V, Fe, Pt, Ir, Os, Pd, Ti, Th, Ge, Hg, Ga, Cr, and Ni are known to crystallise in the cubic system; their crystal structures are therefore appropriately represented by the cubic closest-packed assemblage of equal spheres. It must not, however, be concluded that for this reason all the spheres composing the structure are identically treated in the packed assemblage; some, selected homogeneously, might be differently treated from others and the assemblage yet exhibit holohedral, hemihedral, or tetartohedral symmetry of the cubic system according to the particular type of homogeneous distribution of the preferentially treated spheres.

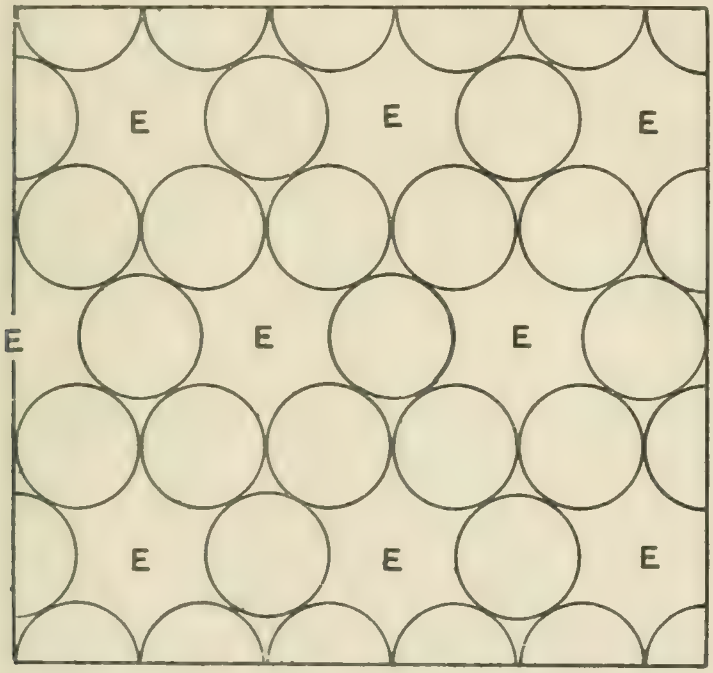
The elements Mg, Zn, Cd, Gl, C, As, Sb, Bi, and Te crystallise in the hexagonal system or in one of its sub-divisions and exhibit the axial ratios stated in the accompanying Table II. As is to be expected the axial ratios approximate more or less closely to those of the closest-packed hexagonal assemblage of equal spheres, namely, to $a:c = 1:1{\cdot}6330$ or $1:1{\cdot}4142$; this is indicated in the table.

TABLE II.

	Axial ratios. $a : c$.	Approximating to the form
Glucinum	1 : 1·5802	1·6330
Magnesium	1 : 1·6242	,,
Zinc	1 : 1·3564	1·4142
Cadmium	1 : 1·3350	,,
Arsenic	1 : 1·4025	,,
Antimony	1 : 1·3236	,,
Bismuth	1 : 1·3035	,,
Tellurium	1 : 1·3298	,,

The assemblages appropriate to these elements are therefore not dimensionally identical with the closest-packed assemblage of equal spheres, but may be regarded as made up of spheres of slightly differing sizes, representing some preferential treatment of a proportion of the atoms; they may, however, be regarded as having the marshalling of the assemblage referred to.

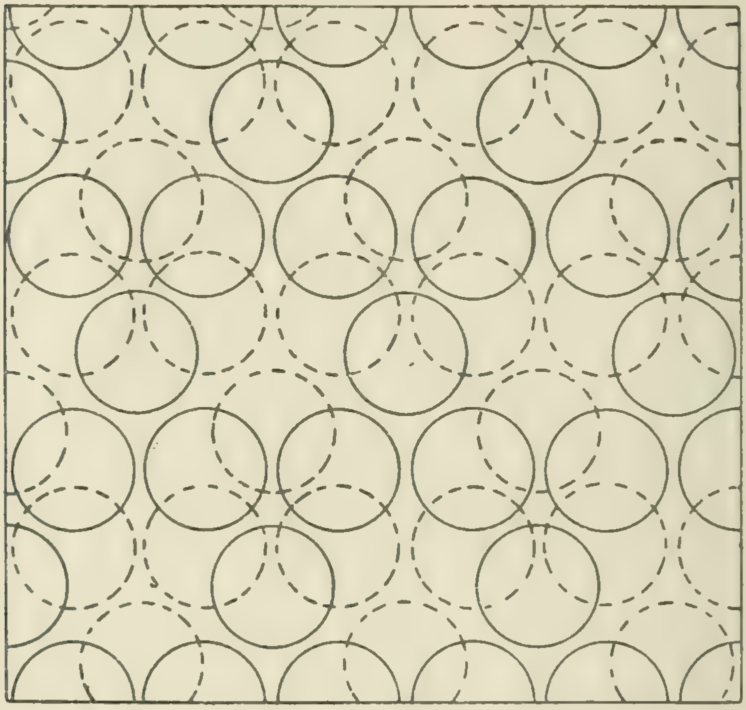
FIG. 9.



In the case of glucinum, which shows $a : c = 1 : 1·5802$ (Brögger and Flink, *Zeitsch. Kryst. Min.*, 1884, **9**, 228), it is clear that the structure is closely related to the model hexagonal assemblage; the appropriate assemblage may be more exactly imitated by very slightly expanding every fourth sphere in a layer of Fig. 5 in the closest-packed hexagonal assemblage of equal spheres. The expanded spheres are symmetrically selected so that each is in contact with twelve unaltered spheres and have their centres at the points marked *E* in any one layer as shown in Fig. 9. The packing may then be made close by slightly pressing together these layers, which lie perpendicular to the principal or c axis, whilst leaving the a axis unchanged. The resulting assemblage can be regarded as made up of columns of triads of unaltered spheres (Fig. 10) such as occur in benzene (Trans., 1906, **89**, 1701), the expanded spheres, which are omitted from both diagrams, being fitted in between these columns; the figure much exaggerates the change needed. If in the original assemblage exhibiting $a:c = 1:1{\cdot}6330$ the described slight expansion of one-fourth of the constituent spheres occurs, it can be made of such a magnitude that the axial ratio becomes $a:c = 1:1{\cdot}5802$.

The same kind of construction serves for magnesium, which exhibits the axial ratios $a:c = 1:1{\cdot}6242$ (Hlawatsch, *Zeitsch. Kryst. Min.*, 1900, **32**, 497), but, as this axial ratio is nearly identical with that of the unmodified assemblage, namely, $a:c = 1:1{\cdot}6330$, the requisite amount of expansion of one-fourth of the constituent spheres is almost infinitesimal.

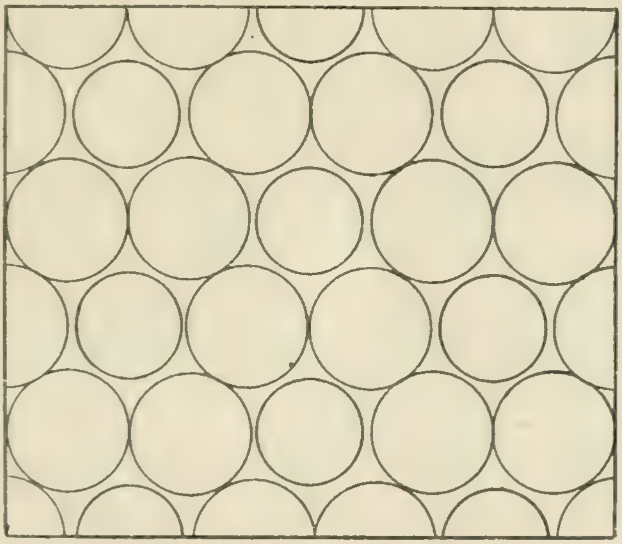
FIG. 10.



The axial ratios of Zn, Cd, As, Sb, Bi, and Te quoted in Table II must be regarded as representing the alternative form of ratio for the hexagonal closest-packed assemblage in which $a:c = 1{\cdot}4142$; the same kind of preferential treatment of every fourth sphere, leading to its slight expansion, as has just been described, will adjust the axial ratio of the model assemblage to that actually observed. As antimony and bismuth are trigonal, and apparently ditrigonal, it is indicated that the disposition of the preferentially treated spheres is such as to give trigonal and not hexagonal symmetry. In addition to the trigonal form with $a : c = 1 : 1{\cdot}4025$ which arsenic affects, a cubic form is also known; the assemblage for the latter is derived from that of the former by so orientating the same layers, those, namely, which lie perpendicular to the trigonal axis, that the centres of the expanded spheres form a cubic space lattice.

The pseudo-cubic trigonal form with $\alpha = 85°6'$, exhibited by graphite (Kenngott, *Sitzungsber. K. Akad. Wien.*, 1854, **13**, 469), can be derived from the kind of structure already depicted (Trans., 1906, **89**, 1742) by expanding every fourth sphere as described above; the crystallographic data available are, however, not sufficiently complete to enable this case to be satisfactorily discussed.

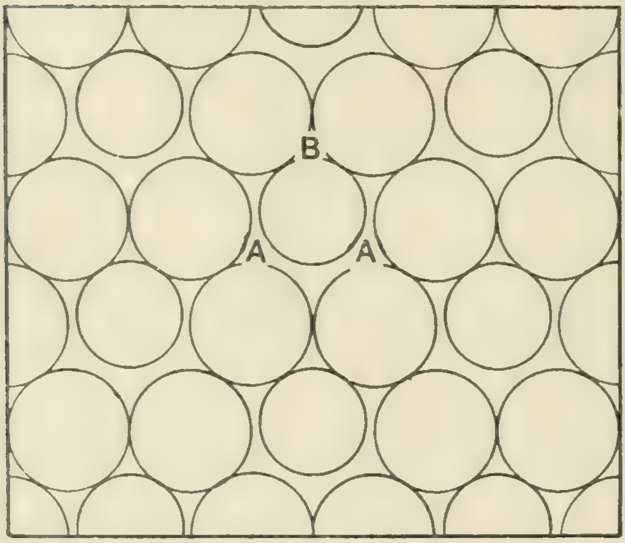
FIG. 11.



Of the crystalline forms of the elements which are neither cubic nor hexagonal, those of sulphur have been most completely examined; we have to show how these and other crystalline assemblages of elementary substances can be related to the cubic and hexagonal closest-packed assemblages through the fourth geometrical property of such assemblages. The ordinary orthorhombic form of sulphur exhibits the axial ratios $a : b : c = 0{\cdot}8108 : 1 : 1{\cdot}9005$ (Brezina, *Sitzungsber. K. Akad. Wien*, 1869, **60**, 539) and may be derived from the hexagonal closest-packed arrangement of equal spheres in the following manner.

Slightly shrink each third sphere, selected symmetrically as indicated on an exaggerated scale in Fig. 11, in each layer of spheres lying perpendicular to the principal axis of symmetry; if the dimensions of the assemblage remain unchanged, the spaces allotted to the shrunken spheres will now be too large and the packing can be rendered closer by the following adjustment. Each of the smaller spheres in the layers is caused to move in the same direction until it touches two of the unaltered spheres of its layer as indicated in Fig. 12; simultaneously the hexagonal chaplets of larger spheres which enclose the smaller are distorted until each of the latter touches two more, or four in all, of the larger spheres. The change thus effected leads to the production of hollows of different sizes. In placing a similar layer on the one described, large hollows *A* can now be associated with small hollows *B* to receive the spheres; they will then be appropriate for the reception of the large and small spheres respectively, since the former are just twice as numerous as the latter. When layers are packed together in this manner according to the marshalling of the hexagonal closest-packed assemblage, the resulting arrangement exhibits holohedral orthorhombic symmetry. Further, the three axial directions are defined by the symmetry as those of the perpendicular to the layer of Fig. 12, and of the two directions of two-fold symmetry parallel to the edges of the diagram. It is found by calculation that if deformable incompressible spheres are used, a diminution in the volume appropriated by one-third of the spheres, selected as described, amounting to considerably less than 1 per cent., suffices to alter the dimensions of the assemblage when equilibrium is reached to those represented by the axial ratios, $a:b:c = 0{\cdot}8108:1:1{\cdot}9005$, of the orthorhombic modification of sulphur.

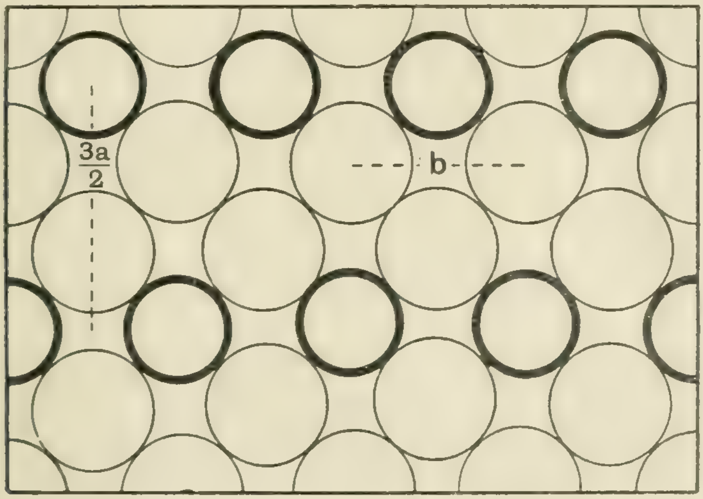
FIG. 12.



On distorting the triangularly arranged layer shown in Fig. 12 so that it becomes the square arrangement shown in Fig. 13, and superposing upon it another similarly distorted layer of the same orientation, the larger spheres of the second layer will appropriately occupy hollows which, in the first layer, are bounded by two small spheres. The structure composed of the two layers now possesses a plane of symmetry in but one direction, that, namely, which is perpendicular to the direction marked *b* in Fig. 13; the addition in a similar manner of other layers leaves the symmetry that of the holohedral monosymmetric system. If in this assemblage the spheres were all of the same size, the axial ratios would be $a:b:c = 1:1:1$, $\beta = 90°$, but a slight diminution in size of one-third of the component spheres selected as indicated would lead to axial ratios of the order of those of the monosymmetric prismatic modification of sulphur, namely, $a:b:c = 0{\cdot}9958:1:0{\cdot}9998$, $\beta = 95°46'$ (Mitscherlich, *Ann. Chim. Phys.*, 1823, **24**, 264). The divergence of the interaxial angle-β from 90° is traceable to similar hollows being dissimilarly occupied in each layer. The assemblage which has been thus obtained has the marshalling of the cubic closest-packed assemblage of equal spheres.

The remaining monosymmetric modification of sulphur which has been crystallographically examined exhibits $a : b : c = 1{\cdot}0609 : 1 : 0{\cdot}7094$, $\beta = 91^\circ 47'$ (Muthmann, *Zeitsch. Kryst. Min.*, 1890, **17**, 336), and appears to result from a distortion of the triangularly arranged layers of Fig. 11 or 12 which causes them to pass to the arrangement shown in the dodecahedral sections of the cubic closest-packed assemblage (Fig. 3) instead of to that of the cube sections of that arrangement (Fig. 4) as in the last described instance. The axial ratios deduced by regarding the cubic closest-packed assemblage of equal spheres from the aspect here suggested are $a : b : c = 1 : 1 : 1/\sqrt{2} = 1 : 1 : 0{\cdot}7071$, $\beta = 90^\circ$; the slight difference between these values and those actually observed and stated above is, as before, attainable by a slight diminution in size of one-third of the component spheres of the assemblage.

Fig. 13.

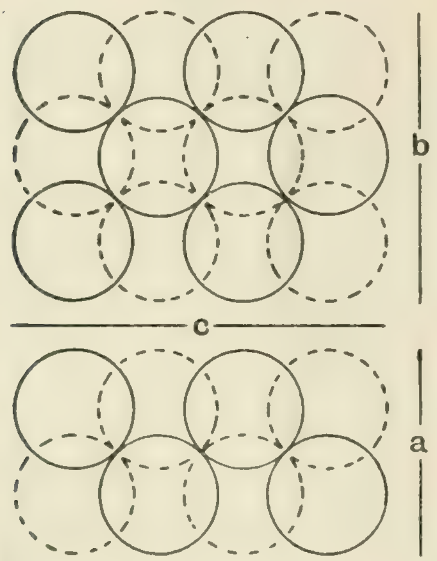


In addition to the foregoing, a trigonal modification of sulphur has been described (Friedel, *Compt. rend.*, 1891, **112**, 834). The superposition of the distorted layers shown in Fig. 12 about a trigonal axis perpendicular to the plane of the layer would lead to the requisite symmetry and to axial ratios comparable with the values $a : c = 1 : 1{\cdot}6330$ or $1 : 1{\cdot}4142$ of the closest-packed hexagonal assemblage of equal spheres. The axial ratios of this modification have, however, not been determined; it is possibly isomorphous with the trigonal modification of tellurium mentioned above.

The ordinary form of selenium is described as holohedral monosymmetric with $a : b : c = 1{\cdot}6349 : 1 : 1{\cdot}6095$, $\beta = 104^\circ 2'$ (Muthmann, *Zeitsch. Kryst. Min.*, 1890, **17**, 354); it has, however, not been previously remarked that by assigning a simpler set of indices to the observed forms this modification may be clearly shown to be pseudo-tetragonal if not pseudo-cubic. On changing the indices of 001, 100, 111, $\bar{1}11$, and 210 to 101, $10\bar{1}$, 110, 011, and $11\bar{1}$ respectively, the axial ratios become $a:b:c = 0{\cdot}9983:1:1{\cdot}2544$, $\beta = 90°23'$. This modification of selenium would thus appear to be morphotropically related to the monosymmetric form of sulphur which shows $a:b:c = 0{\cdot}9958:1:0{\cdot}9998$, $\beta = 95°46'$, and may hence be accounted for in a similar manner.

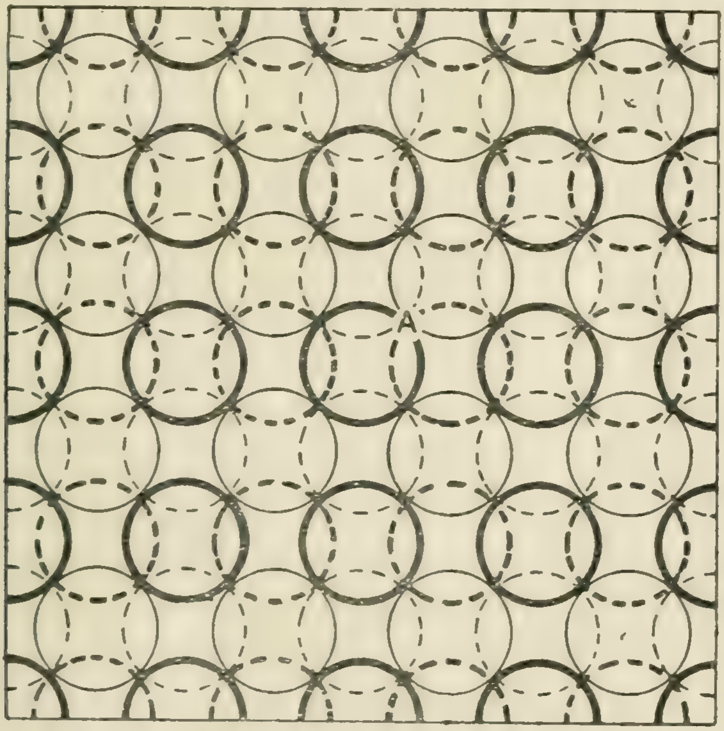
Iodine crystallises in the orthorhombic bipyramidal system with the axial ratios $a:b:c = 0{\cdot}6644:1:1{\cdot}3653$ (Mitscherlich, *Sitzungsber. K. Akad. Berlin*, 1855, 411); these values are very striking inasmuch as they are, almost within the limits of experimental error, in the ratio of $a:b:c = 2:3:4 = 0{\cdot}6667:1:1{\cdot}3333$. If the cubic closest-packed assemblage of equal spheres is built up from rectangular blocks of twelve spheres, measuring two, three, and four spheres respectively in the three rectangular directions, as shown in plan and elevation in Fig. 14, the axial ratios $a:b:c = 2:3:4$ would result. The rectangularly arranged blocks in question are fragments of the cubic closest-packed assemblage cut therefrom in directions parallel and perpendicular to its cubic section (Fig. 4), and can be packed together so as to form that assemblage. It is clear that a very slight distortion resulting from some very small difference in size between certain of the constituent spheres will suffice to account for the minute divergence of the observed axial ratios from the ratios $2:3:4$. The crystalline structure of iodine thus has the cubic marshalling, but it is not possible to draw conclusions respecting the magnitude of the molecular aggregate which forms the unit of the packing because the rather complicated set of forms exhibited by the crystals would be almost equally simply expressed by reference to pseudo-cubic axial ratios of the values $a:b:c = 0{\cdot}9966:1:1{\cdot}0240$.

Fig. 14.



Two crystalline modifications of tin have been goniometrically examined; a tetragonal, apparently holohedral, form showing $a:c = 1:0{\cdot}3857$ (Miller, *Phil. Mag.*, 1843, **22**, 263) and an orthorhombic bipyramidal form showing $a:b:c = 0{\cdot}3874:1:0{\cdot}3558$ (Trechmann, *Min. Mag.*, 1879, 3, 186). The tetragonal form may be derived from the cubic closest-packed assemblage by making one-half of the spheres of each layer perpendicular to a tetragonal axis (Fig. 15), symmetrically selected, very slightly smaller than the remaining half, and by arranging consecutive similar layers of this kind so that tetragonal screw axes, such as *A*, are produced in such a way that each layer can be located by a movement of the neighbouring layer about the screw axis. If unit length along the a axis is taken as twice the distance between the nearest sphere centres in a layer and that along the c axis as the distance between consecutive layers of centres, and the spheres are all of the same size, $a : c = 2\sqrt{2} : 1 = 1 : 0{\cdot}3535$. The slight difference between this value and that actually observed is obtained by the suggested difference in magnitude of the two kinds of spheres employed.

FIG. 15.



If each layer of the above assemblage is similarly distorted until it acquires the spacing appropriate to a dodecahedral face-layer (Fig. 3), a system is obtained which, if equal spheres are used, can have the axial ratios $a : b : c = \sqrt{2} : 4 : \sqrt{2} = 0{\cdot}3535 : 1 : 0{\cdot}3535$. The axial ratios of the orthorhombic modification of tin would be obtainable by a slight change in size of one-half of the component spheres of the same nature as that which leads to the tetragonal structure.

In the foregoing pages we have discussed practically the whole of the available geometrical data concerning the crystalline forms of the elements and have shown that in every case the crystalline form affected by an element is derived in some simple manner from either the cubic or the hexagonal closest-packed assemblage of equal spheres; the nature and magnitudes of the departures from the model assemblages have been explained by the aid of the fourth geometrical property and the supposition that certain component atoms of the structure secure slightly preferential treatment during crystallisation. A working scheme is thus provided which embraces the crystalline forms of all the elements so far as they are known.

So far as the authors are aware, the close parallel which is thus shown to exist between the two closest-packed assemblages of equal spheres, on the one hand, and the crystalline forms of the elements, on the other, has not been previously remarked; nor has the minute amount of modification of such assemblages needed to cause them to exactly simulate the crystalline forms of those elements which do not crystallise in either the cubic or hexagonal systems.

One conclusion which may be drawn as a result of carefully considering the crystallographic data available for the elements appears of importance. The trigonal crystals of arsenic with $a:c = 1:1{\cdot}4025$ (G. Rose, *Ann. Phys. Chem.*, 1849, [ii], 77, 146) and those of the hexagonal magnesium with $a:c = 1:1{\cdot}6242$ have been measured with much greater accuracy than any of the other trigonal elements; at the same time the axial ratios given for these elements approximate more closely to the values calculated for the model assemblage than do those of the others. It seems therefore probable that the noted discrepancies, small as they are, are in part due to experimental inaccuracy and will become smaller still as more precise measurements are obtained.

The Crystalline Structure of Binary Compounds.

Most binary compounds are composed of two elements of the same valency, and, according to our previous results, the spheres of atomic influence of two such elements possess approximately the same volume. It follows immediately that binary compounds of two elements of the same valency should, in accordance with the fourth geometrical property, in most cases possess crystalline structures in which the marshalling is that of either the cubic or the hexagonal closest-packed homogeneous assemblages of equal spheres. A reason is thus provided for the well known, but hitherto unexplained, fact that some 88 per cent. of the determined crystalline forms of binary compounds are either cubic or trigonal (see Table I). Practically the only crystalline forms of binary compounds known to belong to other than the cubic or trigonal systems are those of the tetragonal mercurous chloride and iodide and silver fluoride, the orthorhombic litharge, PbO, and iron arsenide, FeAs, and the monosymmetric mercuric oxide, HgO, arsenic sulphide, AsS, and cupric oxide, CuO; the crystalline form of silver fluoride is doubtful, and some of the other substances just noted are composed of two elements of different valencies. The known facts are consequently expressed by the statement that practically all binary compounds composed of elements of the same valency crystallise in either the cubic or the hexagonal systems, most, however, belonging to a hemihedral or tetartohedral class of one or other system. The following table (Table III) includes all those binary hexagonal subtances which have been crystallographically examined, and which undoubtedly consist of two elements of the same valency.

TABLE III.

	$a : c.$		$a : c.$
GlO *	1 : 1·6305	CdS ¶	1 : 0·8109
ZnO †	1 : 1·6077	AgI ‖	1 : 0·8196
ZnS ‡	1 : 0·8175		

* Mallard, *Ann. des Mines*, 1887, **12**, 427.
† Traube, *Jahrb. Min.*, *Beil.-Bd.*, 1894, **9**, 147.
‡ Friedel, *Compt. rend.*, 1861, **52**, 983.
¶ Mügge, *Jahrb. Min.*, 1882, **2**, 1.
‖ v. Zepharovitch, *Zeitsch. Kryst. Min.*, 1880, **4**, 119.

The measurements from which the above axial ratios are calculated may be regarded as fairly accurate; they differ so slightly from those for the closest-packed assemblage of equal spheres, namely, $a:c = 1:1·6330$, or one-half that ratio, $a:c = 0·8165$, that they may be considered as practically identical with the value for the model assemblage.

Whilst it must be conceded that the above discussion of the crystalline forms exhibited by the binary compounds of elements of the same valency furnishes a definite proof, independent of our previous demonstration, that in a crystalline structure the constituent elements appropriate spheres of influence approximately proportional in volume to their fundamental valencies, it must be noted that these binary compounds do not in every case exhibit holohedral symmetry. Holohedrism is generally observed among the elements, but apparently occurs only rarely among the binary cubic compounds; the occurrence of hemihedrism or tetartohedrism among the latter is attributable to the condition that the assemblages have to be constructed from spheres of two appropriately different, although nearly equal, sizes and that the symmetrical arrangement in equilibrium of the two sizes of spheres must in many instances give rise to hemihedral or tetartohedral symmetry.

It is desirable to extend this enquiry to a detailed investigation of several typical binary compounds for the purpose of determining whether our method accounts, not only for the general marshalling or the crystalline system affected, but also for the particular hemi- or tetartohedral crystal class to which they belong. During this extension, it will be incidentally shown that the theory provides a simple explanation of the occurrence of polymorphism, and also of a number of other crystallographic properties of the substances concerned which have hitherto received no explanation.

Silver Iodide.

Silver iodide is dimorphous, crystallising at the ordinary temperature in the hemimorphous pyramidal class of the hexagonal system with $a:c = 1:0·8196$, whilst at 145—147° it undergoes conversion with almost explosive violence into a cubic modification (Lehmann, *Zeitsch. Kryst. Min.*, 1877, 1, 492). It has already been pointed out (p. 1169) that these two crystalline modifications are almost exactly simulated by the cubic and hexagonal closest-packed assemblages of equal spheres, and in view of the close approximation of the axial ratio for the hexagonal silver iodide to that of the latter assemblage, the spheres of atomic influence of silver and of iodine will naturally be regarded as of almost the same size.

A geometrical distribution of two kinds of nearly equal spheres in equal numbers, representative of the cubic modification of silver iodide, is derivable in the following manner from the closest-packed cubic arrangement of equal spheres.

Partition space into equal cubes distinguished as of two kinds, black and white, present in equal numbers, the cells of one kind being in contact along edges only, as indicated in Fig. 16. Describe small equal spheres about the centres of the cube cells of one kind, say the black, and cause all these spheres to expand uniformly until they touch their next neighbours. A comparison of Figs. 16 and 4 will show that the system of spheres thus obtained is the cubic closest-packed arrangement, for the centres of the spheres in Fig. 4 lie at the centres of one-half of the cube cells of a certain cubic partitioning of space, chosen so that the selected cubes are in contact along edges only.

Next effect an auxiliary partitioning of the system of Fig. 16 into larger cubes, each containing eight of the small cubes, four of each colour tetrahedrally arranged, and treat these large cells of the partitioning in the same way as before, namely, distinguish them as of two colours, say red and blue (*R* and *B*, Fig. 17), those of one colour

Fig. 16.

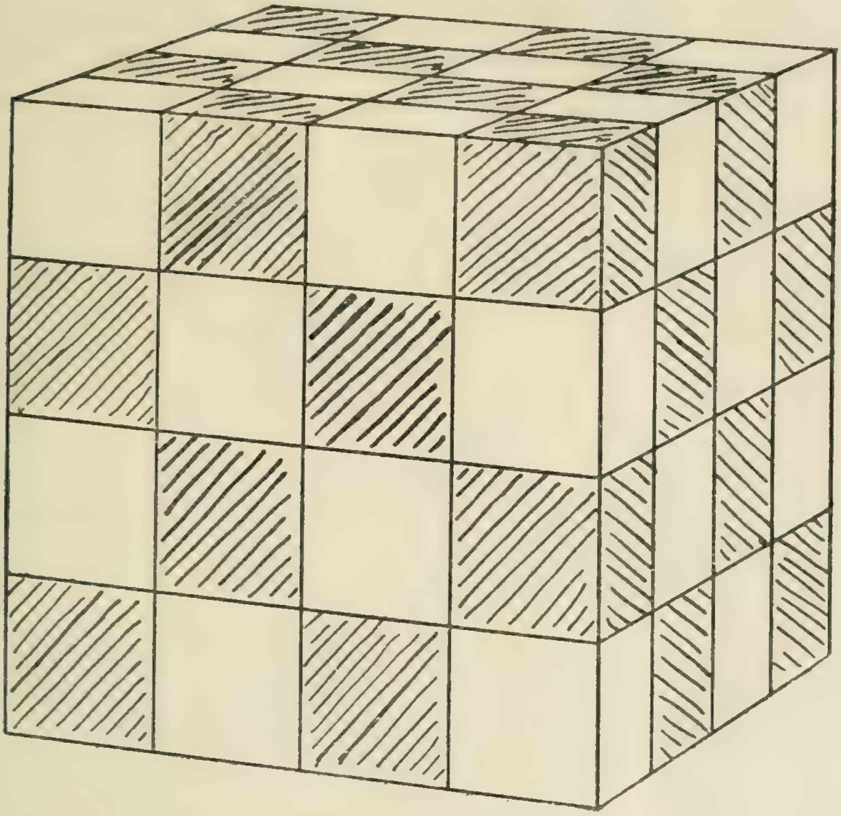
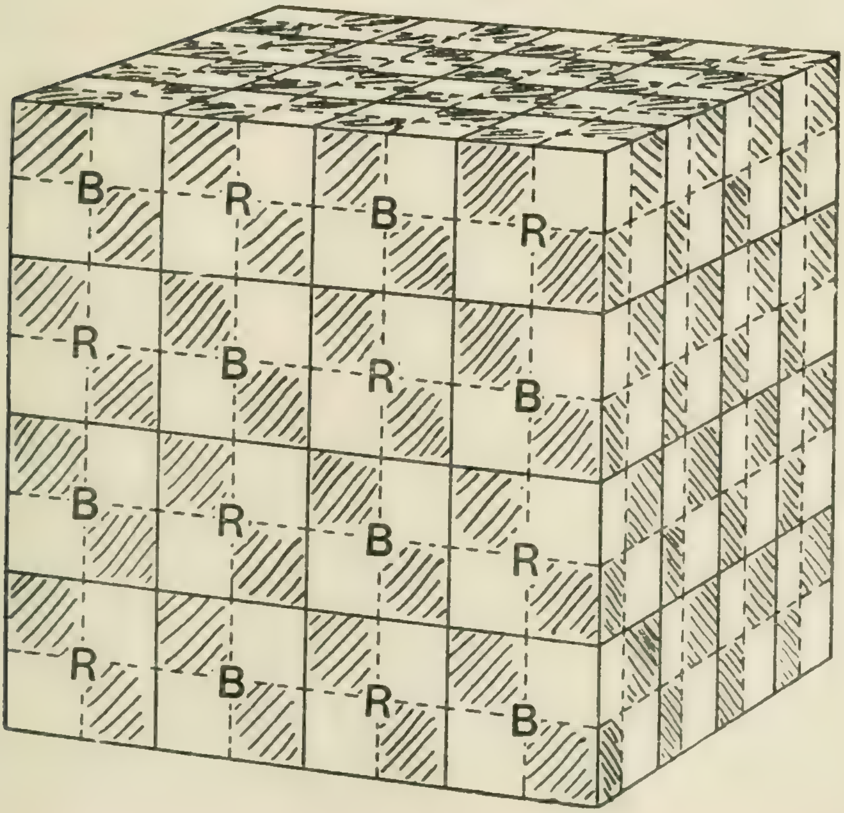


Fig. 17.



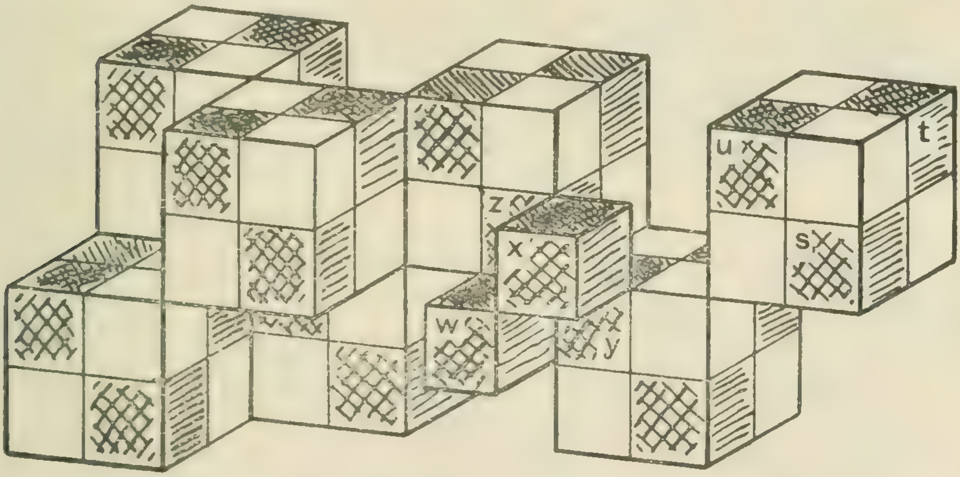
being in contact along edges only; distinguish the tetrahedral groups of spheres having their centres in the large cells of the partitioning in the same manner, so that corresponding to the large red and blue cells, the contained tetrahedral groups of four spheres are coloured red and blue respectively. The two kinds of spheres which are thus distinguished as having their centres within the red or the blue cells of the partitioning are, after modification as described below, to represent the spheres of atomic influence of silver and iodine respectively. The large cell partitioning indicates a division of the assemblage into tetrahedral groups of spheres, because each large cell contains four centres of spheres arranged tetrahedrally; all the tetrahedra thus derived are similarly orientated.

Since each sphere in the closest-packed cubic arrangement is, as seen from Figs. 2 and 4, in contact with, and similarly related to, twelve surrounding spheres, there are several ways in which it can, in conjunction with three of them, form a tetrahedral group; even when two sets of spheres have been distinguished in the manner just described there are still several ways in which the spheres of a set, red or blue, can be allotted for the purpose of forming tetrahedral groups. The results obtained in these cases are, however, identical with one or other of two kinds of group formation; one is the kind described above, in which the two sorts of tetrahedra are similarly orientated; the other is a distinct kind of partitioning into oppositely orientated tetrahedra, those of one orientation being composed of spheres whose centres lie in red cells, and those of the other consisting of spheres centred in the blue cells.

On examining by itself the assemblage formed of one set of the tetrahedral groups, that, for instance, the centres of which are contained in the set of red cubes, it is found that partitioning into tetrahedral groups can take place in two ways, the groups obtained by the one method having an orientation opposite to that of those obtained in the other. This is seen on considering the set of red cubes by themselves, as shown in Fig. 18. For in place of the above described partitioning into large cubic cells, let a similar partitioning be effected in which the partitioning planes pass midway between those of the first partitioning; the eight small cubes, four white and four black, which go to form each new large cell, belong to eight large cells of the previous partitioning. Fig. 18 shows a number of the original red cells of the cube partitioning, in which the tetrahedral sphere groups have the orientation r, s, t, u, but on selecting as a tetrahedral group of spheres a set of the kind w, x, y, z, one being taken from each of four different large red cells of the original partitioning, it is seen that the latter tetrahedral group is oppositely orientated to the former. As this choice of two partitionings, giving two opposite orientations, is applicable both to the red and the blue tetrahedral groups, it is evident that a division of the entire assemblage may be made either into red and blue tetrahedral groups of spheres of the same orientation or of opposite orientations. Whilst, therefore, the original partitioning of the assemblage as a whole into large red and blue cube cells leads to its consideration as a closest-packed intercalation of red and blue tetrahedra of spheres of identical orientation, the second method of combining the results of the alternative partitionings leads to its being regarded as an intercalation of sets of red and blue tetrahedra of spheres in which the latter are oppositely orientated with respect to the former.

On considering the plan (Fig. 2) of the octahedral sections of the original cubic assemblage of equal spheres in conjunction with the present assemblage in which the spheres are distinguished as of two

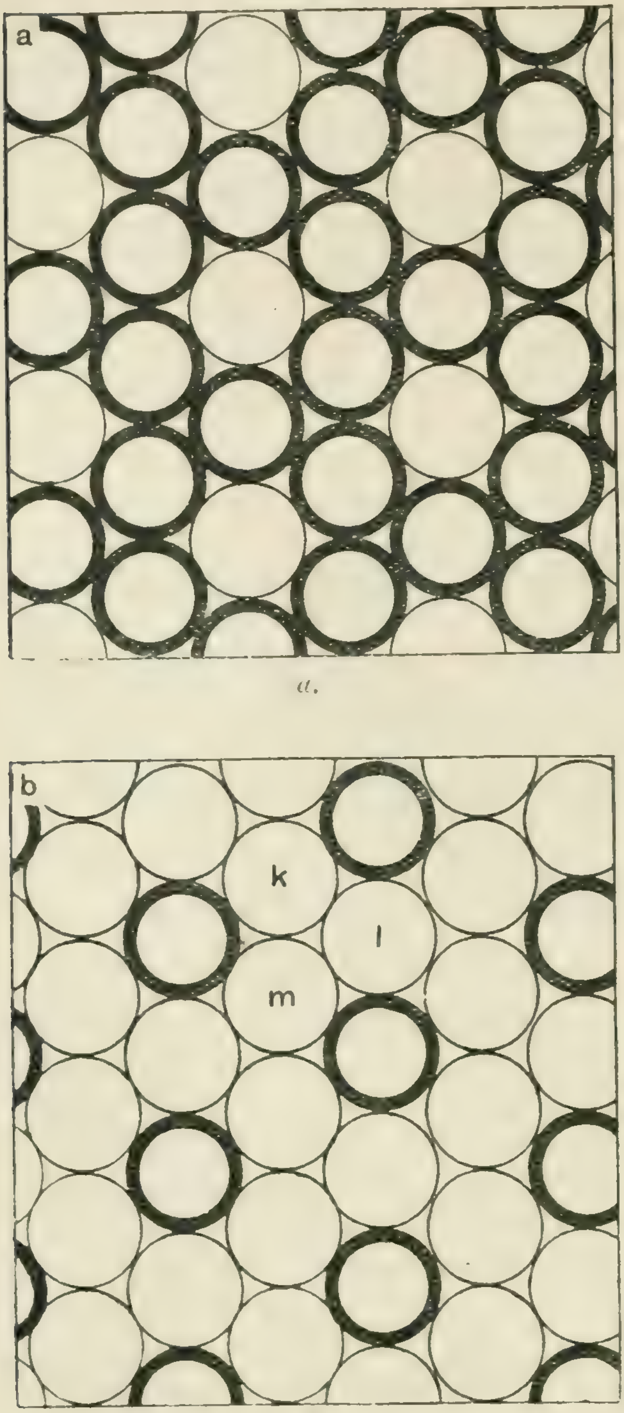
FIG. 18.



kinds, it will be seen that the projections of six layers, instead of three only, are now distinguishable. Thus, six sections (Fig. 19, *a*, *b*, *c*, *d*, *e*, and *f*) have now to be superimposed in order to represent the projection of the entire assemblage upon the octahedral plane; in this figure the spheres of one colour, red or blue, are shown as heavily lined circles, those of the other as lightly drawn circles.

As a result of the foregoing discussion, it follows that from the cubic closest-packed assemblage of equal spheres may be derived an assemblage possessing cubic symmetry, consisting of two kinds of equal spheres in equal numbers; each sphere is so situated with respect to nearest spheres of the same kind that it can, in conjunction with some of them, form a tetrahedral group in two ways, giving oppositely orientated tetrahedra. Every sphere has the same situation with respect to the rest of the system and its centre is a centre of symmetry and lies both on trigonal and digonal axes. The symmetry is consequently very high, being that of type $9a_1$ of Barlow's list (*Zeitsch. Kryst. Min*, 1894, 23, 45), and the crystallographic symmetry is that of the holohedral cubic system.

Fig. 19.



a.

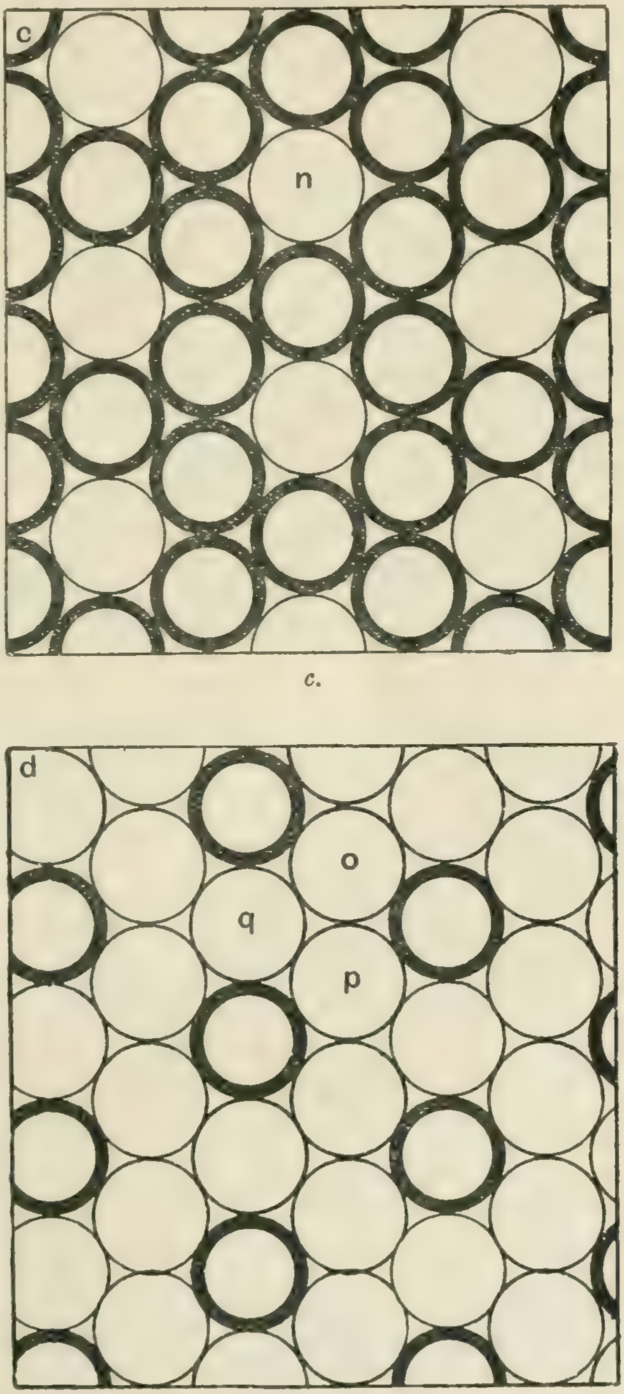
b.

It is not known to what class of the cubic system silver iodide belongs, and, in view of the fact that the closeness of the axial ratio of the hexagonal modification to that presented by an hexagonal assemblage of equal spheres suggests that the spheres of atomic influence of silver and iodine are of nearly the same volume, it will for the present suffice to advance the above as representing very closely the crystal structure of the cubic silver iodide; the effect produced in the above assemblage by making one kind of sphere slightly smaller than the other is discussed later in connexion with the alkali halogen salts.

The assemblage corresponding to the hexagonal hemimorphous modification of silver iodide is closely related to the foregoing cubic assemblage, and is derived from it in the manner described below.

An examination of Fig. 19 shows that any two consecutive layers of the cubic assemblage which lie perpendicular to an axis of threefold symmetry can be regarded as consisting collectively of two kinds of oppositely orientated tetrahedral groups of four similar spheres, vertices of the one kind of group pointing downwards, and those of the other pointing upwards; the two kinds of tetrahedral groups are those having their sphere centres in red or in blue cells of the partitioning respectively, and the one kind represents tetrahedra of silver spheres of atomic influence, the other represents the iodine atoms. Such a composite layer is hemimorphous in a direction perpendicular to its plane, although the cubic assemblage of which it forms a stratum possesses holohedral symmetry.

Fig. 19.

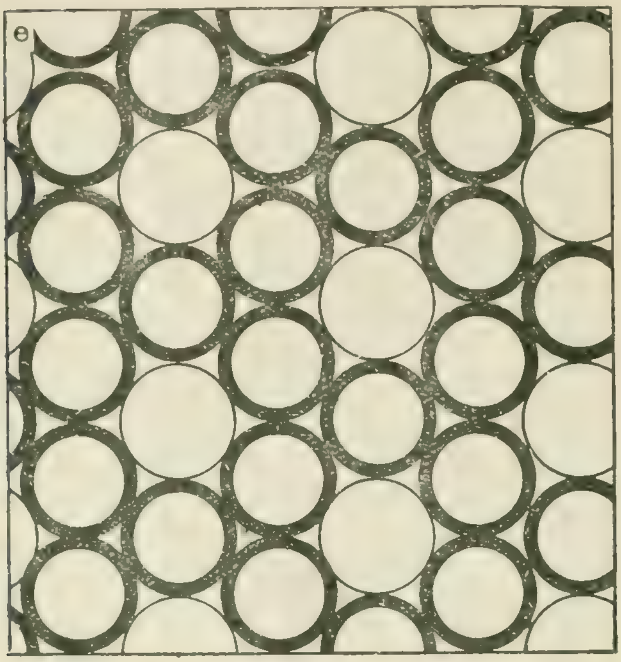


c.

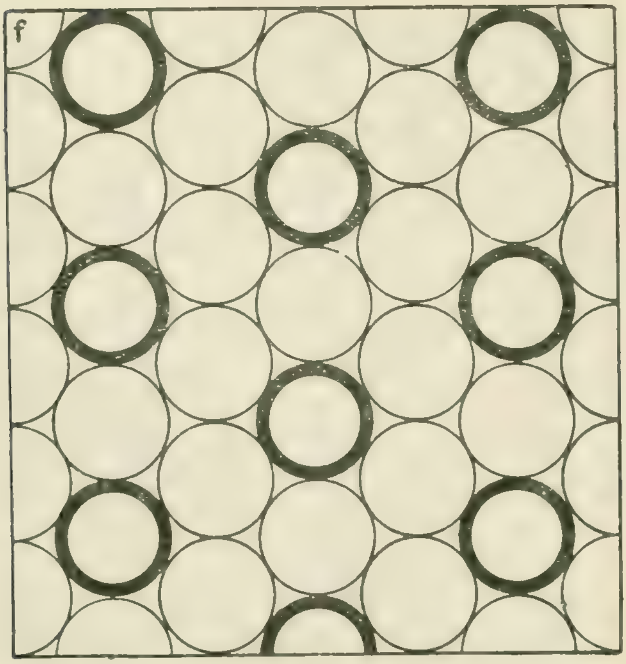
d.

Through the centre of a tetrahedron of either of the two kinds draw a perpendicular to the plane of such a composite layer; make this perpendicular a hexagonal screw axis of such a nature as to locate a second composite layer identical with the first and fitting closely on to it, the two composite layers differing in orientation by 60°. Succeeding similar operations about the same axis will locate other similar layers and complete the assemblage, which will then contain a flock of hexagonal screw axes passing through the centres of all the tetrahedra of the one kind in any composite layer. The relative arrangement of the spheres in the assemblage thus obtained is a mixture of the cubic and the hexagonal closest-packed arrangements of equal spheres already described. Thus a stratum consisting of three consecutive single layers, the middle layer of which has its less numerous spheres transfixed by the hexagonal screw axes, will present the cubic form of arrangement, whilst, where these axes pass midway between the more numerous spheres of the middle layer, the stratum will have the arrangement characterising the hexagonal form of closest-packing. The packing has the same maximum degree of closeness as in the case of either of the two simple modes of closest-packing provided that the spheres are all equal in size. The completed hexagonal assemblage, like the composite layer from which it is generated, is hemimorphous, but possesses planes of symmetry.

FIG. 19.



e.



f.

The practical identity of the axial ratio for the hexagonal silver iodide, namely, $a:c = 1:0{\cdot}8196$, with that of the closest-packed hexagonal arrangement of equal spheres, namely,

$$a:c = 1:2 \times 0{\cdot}8165,$$

would seem to indicate the practical identity in volume of the spheres of atomic influence of silver and iodine. It does not, however, absolutely prove this, because it really means that the spacing of the consecutive layers in the composite assemblages of the two dimorphous forms is the same; this similarity of spacing might conceivably accompany a slight difference in volume between the two kinds of sphere of influence. The sudden passage of hexagonal silver iodide to cubic symmetry at 145° may be attributed to a change, probably very slight, in the relative volumes of the spheres of atomic influence of the two kinds produced by change of temperature, as a result of which stable equilibrium occurs in the cubic arrangement at above 145° and in the hexagonal arrangement below that temperature.

It will be seen from the foregoing argument that the conversion of the cubic into the hexagonal modification necessitates a simple and small shear or translation of pairs of the consecutive layers of Fig. 19 over each other, and that the dimorphism of silver iodide consists merely in the existence of alternative methods of close-packing structural units which are dimensionally identical at the transition temperature. This result is of importance as affording a generally applicable explanation of polymorphism, a subject which has hitherto remained almost entirely unelucidated. Polymorphism may, in fact, be defined as the existence of alternative methods of homogeneously close-packing spheres of atomic influence under the condition that the homogeneous partitioning shall yield units or molecules identical in composition, constitution, and configuration. It differs from isomerism in that the latter consists in the existence of alternative methods of close-packing spheres of atomic influence under the condition that the homogeneous partitioning shall yield units or molecules identical in composition but not in constitution and configuration (compare *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 575, 590, 623).

It has been suggested above that the close approximation of the axial ratio of the hexagonal form of silver iodide to that of the closest-packed hexagonal assemblage of equal spheres indicates approximate equality in size of the spheres of atomic influence of silver and iodine ; as already remarked, the practical equality of these magnitudes indicates that each layer of spheres represented in Fig. 19 has all its sphere centres in the same plane. This may have an important bearing on the unique thermal expansion of the hexagonal silver iodide ; Fizeau (*Comp. rend.*, 1864, **67**, 314) and Rodwell (*Phil. Trans.*, 1883, **173**, 1134) have shown that this substance has a negative coefficient of cubic thermal expansion and that the coefficient of linear expansion is large and negative in the direction of the principal axis and small and positive in sign in the directions perpendicular thereto. It is conceivable that the very small excess over the ideal value for the principal axis indicated by the observed axial ratio $a:c = 1:0{\cdot}8196$ displayed by silver iodide may be due to a very slight difference in magnitude between the two kinds of sphere of influence concerned. It is evident that a passage from the ideal condition in which the spheres are all equal to one in which the two kinds of spheres show a minute difference in size, instead of producing a lowering of the symmetry may merely cause a diminution in the number of equal pressures, some of those which in the ideal assemblage are equal becoming a little greater and the others a little smaller. Thus, considering a layer in which one-third of the spheres are a trifle smaller than the rest, the pressure between the larger spheres would be slightly increased and that between spheres of different sizes would be slightly diminished. And whilst an increase in size of both kinds of spheres will tend to expand the whole mass, if the increase proceeds at different rates for the two and in such a manner that the two kinds of spheres become more nearly equal, the closer approximation to equality of size will lead to a closer approximation to the closest-packed ideal assemblage and will thus tend towards contraction of the mass as a whole. A very small increase of size of one kind of sphere and a much larger increase of that of the other accompanying a rise of temperature, can consequently lead to the observed negative coefficient of cubic thermal expansion of hexagonal silver iodide if the structure more nearly approaches the ideal closest-packed arrangement of equal spheres as the temperature rises. This kind of explanation is in harmony with the observation quoted above, namely, that the coefficient of linear expansion is large and negative in the direction of the principal axis and small and positive in directions perpendicular thereto. In this connexion, Sollas (*Proc. Roy. Soc.*, 1898, 63, 291) has made the interesting suggestion that in silver iodide the constituent atoms expand at different rates with rise of temperature because the coefficients of cubic expansion of silver and iodine are very different.

A very precise parallel to the dimorphism of silver iodide is found in that of zinc sulphide, ZnS, which also crystallises in a cubic and an hexagonal form, the latter with $a:c = 1:0{\cdot}8175$; the axial ratio of hexagonal zinc sulphide thus approximates closely to the corresponding value for the hexagonal closest-packed assemblage of equal spheres, namely, $a:c = 1:2 \times 0{\cdot}8165$. The explanation of the dimorphism is obviously similar to that given for silver iodide, but it is important to notice that the cubic modification of zinc sulphide displays tetrahedral hemihedrism. This suggests that the tetrahedrally arranged complexes of four sulphur spheres present in the assemblage exert an effect analogous to that attributed (p. 1159) to aggregation in connexion with the crystalline forms of the element itself; the effect in question consists in a lowering of the crystallographic symmetry.

The Halogen Compounds of the Alkali Metals.

In most cases where the atoms of a compound are of different kinds, although of the same valency, the crystalline symmetry is, in accordance with the fourth geometrical property, found to be degraded from that of one or other of the two closest-packed assemblages of equal spheres; the degradation of symmetry may result in the production of a structure belonging to a hemihedral or tetartohedral class of the cubic or hexagonal system of symmetry respectively or of one characterised by the possession of pseudo-cubic or pseudo-hexagonal symmetry. This degradation of symmetry will, in the following pages, be traced partly to the diversity of atoms occupying similar situations in the marshalling, and partly to a distortion due to closest-packing occasioned by the mutual adjustment of the spheres of an assemblage whose marshalling is that of one of the most symmetrical systems referred to and necessitated by the slight difference in magnitude between the spheres. High symmetry of marshalling can in this way coexist with a low symmetry of crystal form, as has been seen in connexion with the crystal form of monosymmetric sulphur, of orthorhombic iodine, and of the hemimorphous hexagonal silver iodide, but it will commonly betray itself either by the close approximation of the crystallographic axial ratios to those characterising the model assemblage to which the arrangement is related or by the crystal habit.

For the purpose of verifying these deductions it is convenient to study those halogen compounds of the alkali metals which crystallise in the gyrohedrally hemihedral class of the cubic system forming Class 29 in Groth's classification. The symmetry of this class consists in the possession of three axes (axial directions) of four-fold symmetry, four axes of three-fold symmetry, and six axes of two-fold symmetry; it differs from that of the holohedral cubic class in that no centre of symmetry or plane of symmetry is present. It must be noted that the halogen compounds of the alkali metals exhibit a well-defined cleavage on {100}, a gliding plane parallel to {110}, and a twinning on {111}; Knop also observed (*Molekularconstitution*, 1867, 46) that the crystal habit of potassium and ammonium chlorides is liable to remarkable modifications when crystallisation occurs from highly impure solutions; under such conditions, the crystals assume a rhombohedral or a tetragonal habit owing to growth proceeding preferentially in the direction of one trigonal or tetragonal axis respectively. Crystals of these elongated habits have been described and figured by Slavík (*Zeitsch. Kryst. Min.*, 1902, 36, 268). The occurrence of this symmetrical aberration under the influence of impurity in the crystallising solution indicates the existence of some kind of structural degradation of symmetry. Any configurational scheme adopted must embrace this peculiarity of structure and also the cleavage, gliding, and twinning; it will be seen from the following pages that our method of treatment provides a simple explanation of these features and also elucidates the isomorphism which exists between the halogen salts of the alkali metals and of ammonium.

The halogen compounds named in Table IV are known to crystallise in the gyrohedrally hemihedral class of the cubic system; the experimental observations make it probable that sodium chloride also crystallises in the same class. A number of other binary halogen compounds crystallise in the cubic system, but these are omitted because they have not been sufficiently studied to allow of a decision being made as to the particular class of the system to which they belong. The ammonium halogen salts are included in the table because they are dealt with later in the present paper.

TABLE IV.

		Twin plane.	Cleavage.	Gliding plane.	Translation direction.
Potassium chloride.........	KCl	111	100	110	$1\bar{1}0$
,, bromide.........	KBr	111	100	110	$1\bar{1}0$
,, iodide	KI	111	100	110	$1\bar{1}0$
Rubidium chloride.........	RbCl	—	100	110	$1\bar{1}0$
,, bromide	RbBr	—	100	—	—
,, iodide	RbI	—	100	—	—
Cæsium chloride............	CsCl	—	100	—	—
,, bromide............	CsBr	—	100	—	—
,, iodide	CsI	—	100	—	—
Ammonium chloride	NH_4Cl	111	100	110	001
,, bromide	NH_4Br	111	100	110	001
,, iodide	NH_4I	111	100	110	$1\bar{1}0$

The cubic assemblage presented above (p. 1170) for silver iodide retains holohedral cubic symmetry so long as the two kinds of constituent spheres representing silver and iodine remain so nearly of the same size that the high symmetry of the cubic holohedrism can be retained consistently with close-packing; when, however, substances of similar chemical type, such as the binary compounds named in Table IV, are found to exhibit gyrohedral hemihedrism of the cubic system, which may be regarded as a degradation of the holohedral symmetry, this distinctive feature is capable of explanation on the assumption of a distinct difference in size of the atomic spheres of influence of the metal and the halogen contained in the compound.

It is therefore necessary to consider the effect upon the close-packing of an assemblage such as that attributed to the holohedral cubic silver iodide which would result from a slight reduction in size of one kind of constituent sphere as compared with the other. If, after such reduction, the larger spheres retain their original relative positions, the closeness of the packing will obviously become impaired and the cavities allotted to the smaller spheres will be too large; the larger spheres must therefore tend to close in slightly upon the smaller ones and the change in symmetry thereby caused must be considered.

An inspection of Fig. 19 shows that each red or blue sphere, n, has contact with six other spheres, k, l, m, o, p, and q, of the same colour, and therefore, so long as the spheres of each colour retain the mutual arrangements of their centres depicted, the larger spheres cannot close in upon the smaller ones without some flattening and increase of pressure at the points of contact. Close-packing of an assemblage of deformable spheres involves, however, the even distribution of pressures; the occurrence of increased pressure in the one-half system only is therefore incompatible with close-packing and is consequently inadmissible. In the symmetrical arrangement depicted in Fig. 19 all the sphere centres lie at points of intersection of trigonal and digonal axes; consequently no slight shift of any of the spheres can occur without causing some degradation of symmetry. It has therefore to be ascertained whether any very slight movements of the constituent spheres are possible, after the postulated change in size of one set of component spheres, so as to increase the closeness of the packing, the degradation of symmetry being of such a nature as still to leave the assemblage in the cubic system, although possibly in one of the non-holohedral classes.

It has been already pointed out that the group centres of each set of tetrahedral groups of spheres taken separately have the arrangement of the centres of one set, red or blue, of large cubes in Fig. 17. The minimum space unit of maximum symmetry of the composite assemblage is therefore obtained by describing about one large cube cell of the partitioning the six cubes of the other colour in face contact with it, and joining the centre points of the latter six with the cube corners of the first, as shown in Fig. 20; to the unit is thus allotted the central cube cell of one colour and one-sixth by volume of each of the six surrounding cube-cells of the other colour, the whole comprising therefore the contents of two cube-cells, one of each colour. The resulting figure is the rhombic dodecahedron made up from an inscribed cube of one colour upon each face of which is erected a right pyramid cut from a cube of the other colour. The volume of the rhombic dodecahedron is twice that of a large cube of the partitioning, namely, of the inscribed cube, and the assemblage may be regarded as composed of a close-packed arrangement of such composite rhombic dodecahedra; rhombic dodecahedra can be packed together in the manner indicated in Fig. 21, so as to fill space without interstices.

Five types of symmetry of arrangement exist which belong to the cubic system and are referable to the rhombic dodecahedron as their minimum space-unit of maximum symmetry; these are types 1, $1a_1$, 3, 4, and 6 of Barlow's list (*Zeitsch. Kryst. Min.*, 1894, 23, 1), and in all of them, except type 6, the trigonal axes do not intersect each other. A slight modification of the assemblage of Fig. 19 which

FIG. 20.

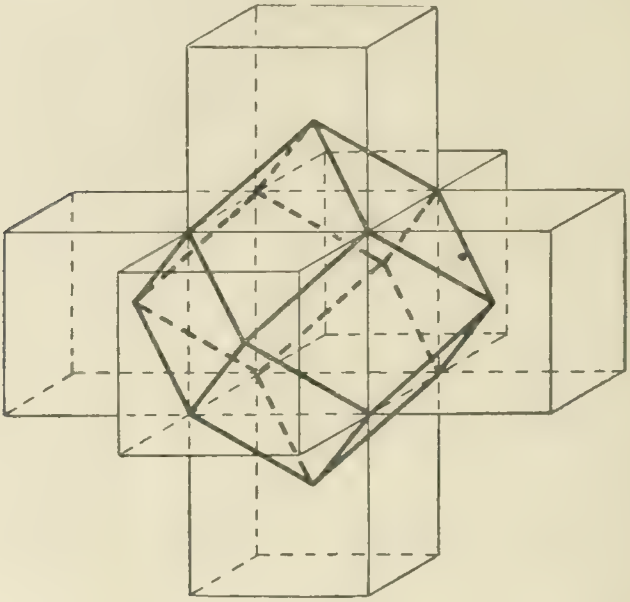
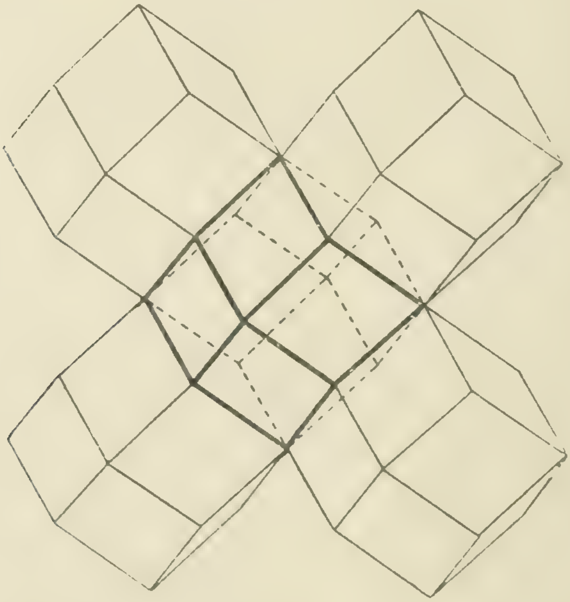


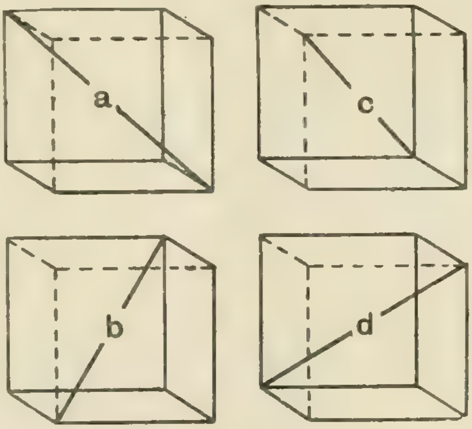
FIG. 21.



causes it to pass to type 3 or type 4, which are enantiomorphously related, restores close-packing after the slight reduction in size of spheres of the one set as compared with those of the other set; the nature of the modification has now to be described.

The disposition of the trigonal axes in types 3 and 4 and in the other types of homogeneous structure belonging to the cubic system which are characterised by the possession of non-intersecting trigonal axes, may be thus visualised (*Zeitsch. Kryst. Min.*, 1894, **23**, 7). In each of two adjoining cells of a cubic partitioning of space effected by three sets of indefinitely extended planes, draw a single diagonal, the directions being so selected that the two lines are not parallel and do not intersect. Produce each line so that it forms a common diagonal of an endless string of the cubic cells joined at opposite corners, these being the corners through which the diagonal passes. By means of rotations through 120° about either of these two diagonals, which are thus used as trigonal axes, locate other diagonals of strings of cubic cells. Repeat this operation of location upon the sets of strings thus generated until as many trigonal axes have been located as can be found by this means. The latter are all common diagonals of strings of the cubic cells and none of them intersects; further, the cells thus generated fill space without interstices, and each is intersected by a single diagonal, the latter being a trigonal axis of the system.

FIG. 22.



The four cube diagonal directions, or directions of trigonal axes, are those named *a*, *b*, *c*, and *d* in Fig. 22; their relative situations in the assemblage are as indicated in Figs. 23*a* and *b*, in which Fig. 23*a* represents the projection of one set of alternate layers of cube cells and Fig. 23*b* that of the other alternate set. The cube cells may be distinguished as of two kinds, *A* and *B*, corresponding to the previous distinction into red and blue cells of the partitioning.

Fig. 24 indicates the manner in which the trigonal axes lie in three rows of one layer of the cube cells. In addition to the trigonal axes referred to and the other elements of symmetry resulting therefrom, types 3 and 4 contain digonal axes of rotation which intersect trigonal axes; the point of intersection of an axis of each of the two kinds is midway between a cell-centre and one of the nearest cell-corners of the system of generating cubic cells.

FIG. 23.

a A	c B	a A	c B	a A
b B	d A	b B	d A	b B
a A	c B	a A	c B	a A
b B	d A	b B	d A	b B
a A	c B	a A	c B	a A

a.

d B	b A	d B	b A	d B
c A	a B	c A	a B	c A
d B	b A	d B	b A	d B
c A	a B	c A	a B	c A
d B	b A	d B	b A	d B

b.

If in the large cube cells of Fig. 17, each of which contains four sphere centres, trigonal axes arranged as in Figs. 23*a* and *b* are distinguished, each large cube cell can possess but one of these trigonal axes of symmetry, and only one of the contained four sphere centres can lie on the selected trigonal axis; the distinction into two kinds of cube cells made in Fig. 17 is applied in Figs. 23*a* and *b* by distinguishing the cells marked *A* from those marked *B*. Fig. 25 depicts a layer of the cube cells of Fig. 23*a* or *b* with the projections of their accompanying spheres; the spheres whose centres lie in two different

FIG. 24.

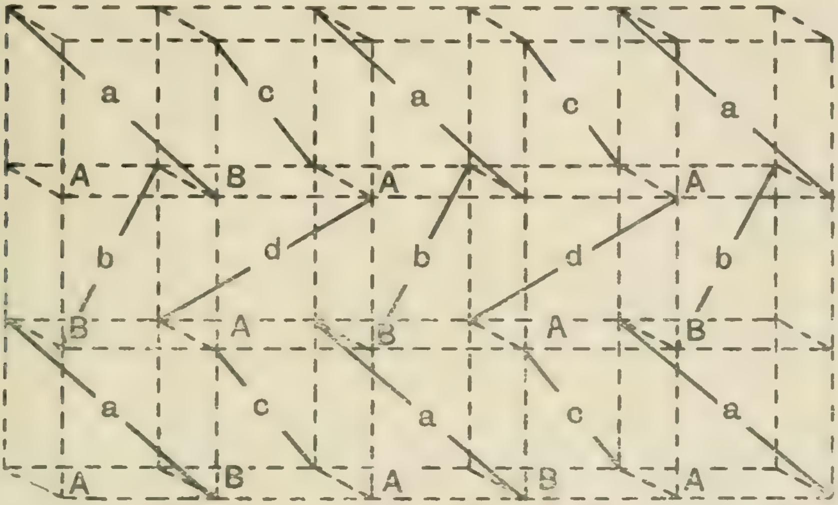
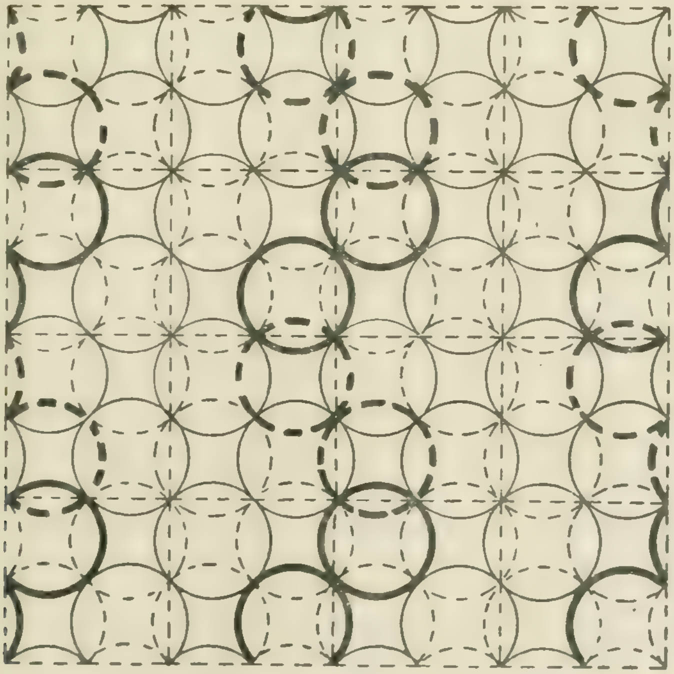


FIG. 25.



planes are distinguished by being represented by continuous and broken circles. The heavy continuous and broken circles represent those spheres which, when the appropriate scheme of non-intersecting trigonal axes of type 3 or 4 is located, will have centres lying on those trigonal axes arranged as in Fig. 23; these sphere centres also lie on the accompanying digonal axes. The spheres whose centres lie on digonal, but not on the selected trigonal, axes are represented by lightly drawn continuous or broken circles, and the boundaries of the large cell partitioning are represented by broken straight lines. The partitioning, as before, divides the assemblage into two sets of cells, red and blue or *A* and *B*, the individual members of either of which are in contact at their edges only; one of these sets of cells contains the centres of one kind of sphere, those which represent the spheres of atomic influence of the halogen, whilst the other set contain the sphere centres of the metallic atomic centres.

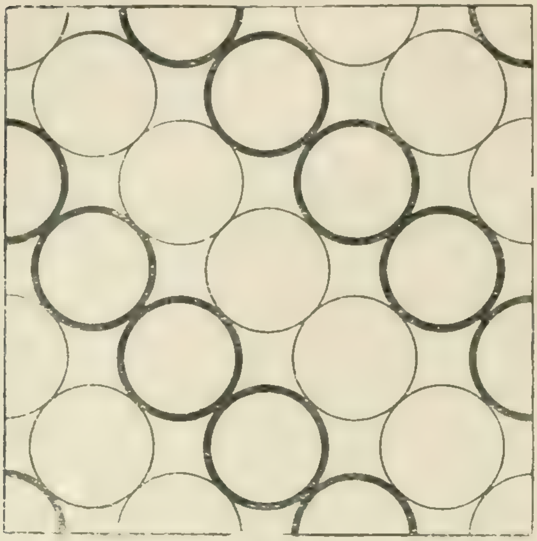
If one kind of sphere becomes appreciably larger than the other kind, the actual arrangement depicted in Fig. 25 cannot be retained consistently with close-packing. Further, any slight shift of those spheres whose centres lie at the intersections of a digonal and a trigonal axis of type 3 or 4 would necessarily destroy one of those axes and hence cause a departure from the symmetry of the type. A slight shift of the remaining three-fourths of the total number of spheres, namely, of those whose centres lie on digonal axes, but not on the selected trigonal axes, may be effected without excluding the type of symmetry referred to, because their sphere centres may move along the digonal axes. A slight rotation of each tetrahedral group of the larger spheres about its selected trigonal axis can be performed which causes the three spheres not centred on the trigonal axis to change their positions slightly on their respective digonal axes without leaving the latter; this slight rotation will not affect the points of intersection of the digonal and trigonal axes which have been selected, but will enable adjacent large spheres of two contiguous cells in the partitioning still to remain in contact, the one sphere moving slightly over the surface of the other. The increase in size of the one kind of sphere and the resulting slight movement will slightly diminish and deform the space available for occupation by the equal number of smaller spheres of the other kind. If the latter diminish in size to such an extent as just compensates the increase in size of the other kind of sphere, the reduced space available for their accommodation will suffice, and by a rotation about their selected trigonal axes, similar to that performed by the larger sphere groups, the tetrahedral groups of smaller spheres are enabled to pack closely within the cavities available for them and, just as before, the digonal and trigonal axes requisite for type 3 or 4 will be preserved.

If therefore in the holohedral cubic silver iodide assemblage of equal spheres of two kinds, represented in Fig. 19, one-half of the spheres selected as there indicated become slightly larger than the others, the assemblage can pass to symmetry of the type 3 or 4 by the loss of three-fourths of its trigonal axes as a result of rotation of the tetrahedral groups of spheres about the remaining one-fourth of the original trigonal axes. The relative positions of the sphere centres lying at the intersections of surviving digonal and trigonal axes remain the same as in the parent simple assemblage, but the distances between adjacent large sphere centres increases, whilst those between neighbouring small sphere centres decrease to a corresponding extent.

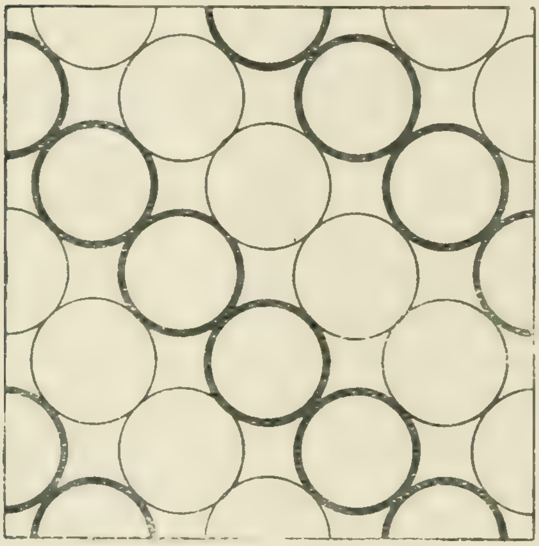
The assemblage of two kinds of spheres of slightly different sizes, arrived at in the manner just described, has the crystallographic symmetry of the gyrohedrally hemihedral class of the cubic system, that, namely, which characterises potassium chloride and the other binary salts named in Table IV. It is consequently suggested that this assemblage actually represents these salts, and confirmation of the substantial accuracy of this conclusion is obtained when the assemblage is examined in connexion with the twinning, the cleavage, and the gliding.

Inspection of Fig. 19 shows that any of the sections of the unmodified assemblage, regarded as of unlimited extent, can have its orientation changed by 60° without its aspect being changed; if, however, such a rotation is given to the structure regarded as composed of the six sections superimposed as described, the aspect of the assemblage as a whole is changed. It follows that the superposition of succeeding layers upon a given layer to form the assemblage depicted in the diagram can take place in either of two ways which present orientations differing by 60°. In consequence of this, a particular layer such as is represented in the figure may belong either to a single assemblage or may be common to two individual assemblages differing in orientation by 60°, and of which it forms the twin plane. The octahedral twinning, such as occurs with the binary compounds of Table IV, would therefore be expected to occur in the described assemblage. In passing from the ideal assemblage of Fig. 19 to the actual assemblage reached by means of the slight change in relative size of the two kinds of spheres and the consequent slight adjustment of the structure, such a common plane of spheres as forms the actual twin plane will doubtless experience some modification which is not related in precisely the same manner to the two orientations of the twinned assemblage. But it may be supposed that a twinned nucleus, the two individuals of which are slightly modified so as to bear the

FIG. 26.

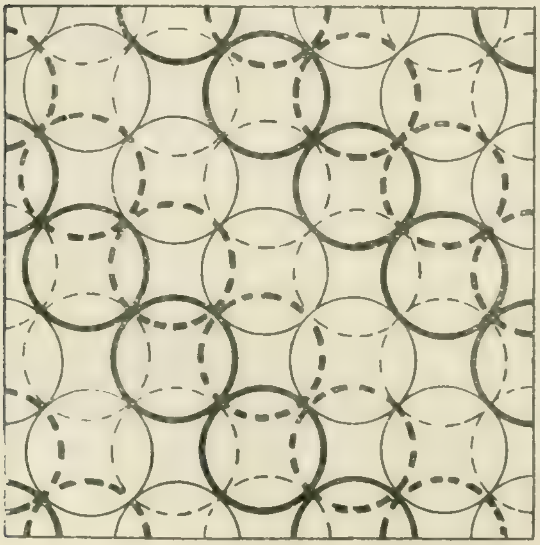


a.



b.

FIG. 27.

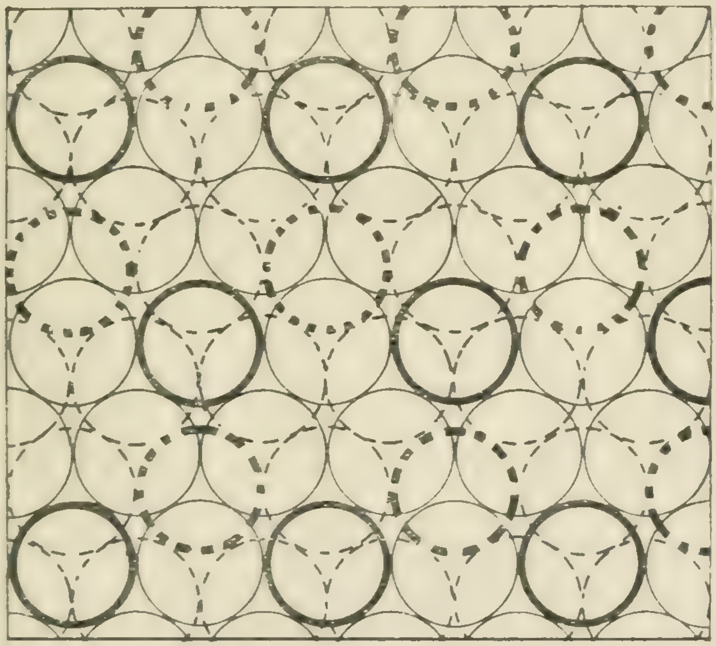


same relation to their twin plane, is first formed, and that after the formation of this nucleus the plane of spheres common to the two orientations does not extend, but that the two individuals grow independently from their respective nuclei, side by side or interlocked, as the case may be. That some slight disturbance and adjustment of the nature suggested is of frequent occurrence is indicated by the common observation that twinned crystals often show re-entrant angles and also generally exhibit morphotropic irregularities and optical anomalies at or near the plane of twinning.

Examination of the unmodified assemblage, or of the stack of large cubes of Fig. 17, reveals that twinning on {100} is also possible in the structure built up of the two kinds of spheres, the twin plane lying midway between two succeeding layers of spheres the projections of which are shown in Figs. 26*a* and *b*. The relative situation of the two layers is shown in Fig. 27; in the twin combination of two layers the diagonal strings of spheres lie parallel instead of crossed as in the single individual assemblage. As twinning of this kind yields no new face directions in the case under consideration, it can effect no modification of face-symmetry, but it will doubtless affect the crystal habit if it occurs to a greater extent in one than in another corresponding direction. The elongation of the crystal habit of potassium chloride in the direction of one cube axis which has been noticed by Knop and Slavík (p. 1179) would be expected to result from this kind of twinning.

A second variety of octahedral twinning is also possible in which the twin plane does not, as in the first variety discussed, pass through a layer of centres contained in the plane (111), but midway between two layers of such centres which have the same, instead of a complementary, atomic composition. The effect of this kind of twinning is shown for two consecutive layers in Fig. 28, and, like that on a cube face, leads to no increase in the number of face-directions; the noted elongation of potassium chloride crystals in the direction of a trigonal axis, which gives the crystal a rhombohedral habit, would be expected to take place if this variety of twinning occurred to a greater extent in the direction of one trigonal axis than of another. The effect of these kinds of cubic and octahedral twinning on the crystal habit is dealt with again in connexion with the ammonium halogen salts (p. 1208).

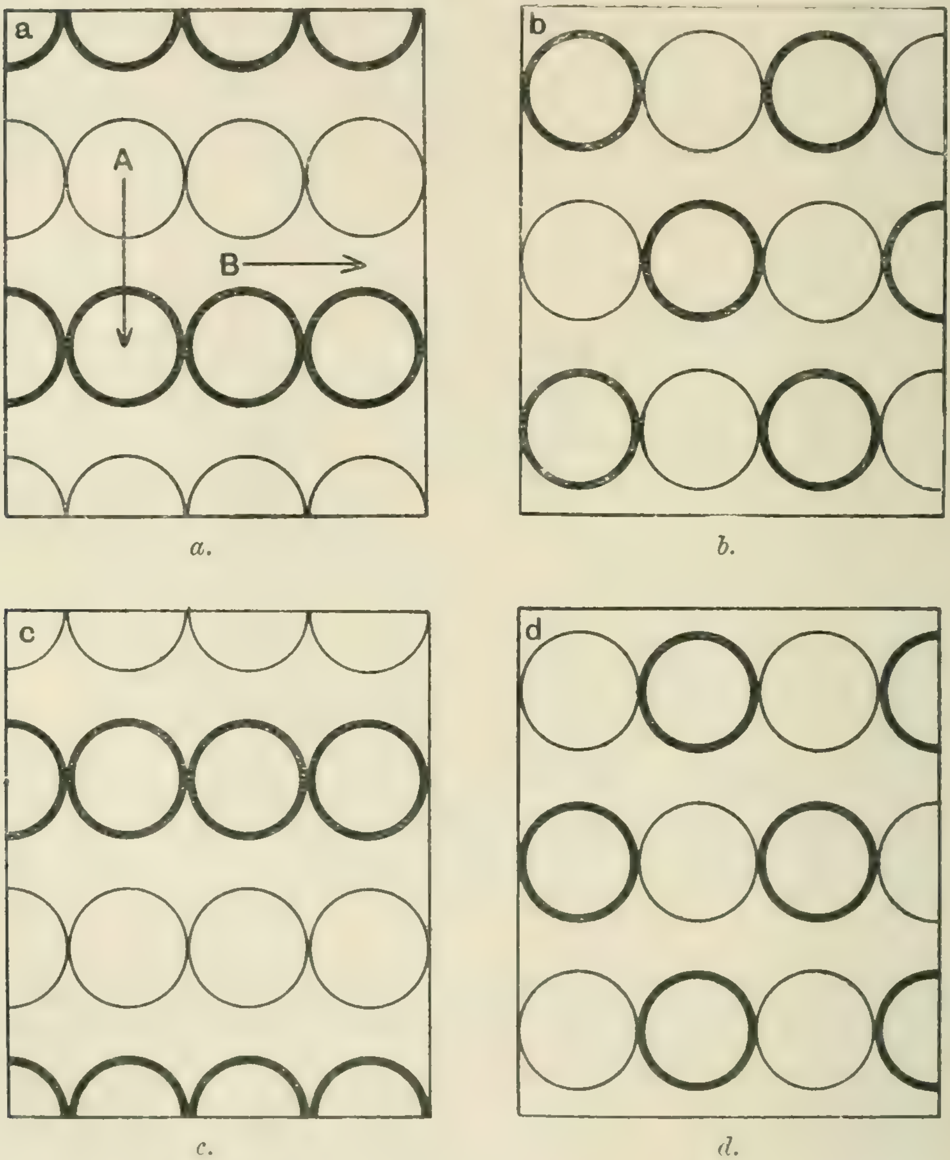
FIG. 28.



It is perhaps significant that the cleavage plane, (100), in these binary salts has the direction of a plane in the assemblage on the opposite sides of which the contiguous parts facing one another are of different compositions, namely, of a plane separating a red cube and its contained red sphere centres from an adjoining blue cube with its contained blue sphere centres. It has been suggested (Barlow, *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 581) that the place of readiest rupture in an assemblage is the place of maximum temporary strain, and that the latter will naturally be some plane which runs between nearest parts of different atomic composition.

In connexion with the gliding planes, plans *a*, *b*, *c*, and *d* of Fig. 29 show the arrangement of four succeeding layers of spheres which are parallel to a dodecahedron face, and on examination it is perceived that a symmetrical distortion which consists in sliding layer upon layer can take place so as to reproduce the original arrangement if the movement occurs parallel to either diagonal of a dodecahedron face, namely, either in the direction of a cube edge or that of a cube face

FIG. 29.



a. *b.*

c. *d.*

diagonal. Thus if *b* is moved along the length of the arrow *A*, and *c* is moved on *b*, *d* on *e*, &c., in a similar manner, the original arrangement of the spheres is reproduced, the effect, considered from a fixed point, being equivalent to a movement of the entire assemblage in a horizontal direction, and this is also the case if *b* is moved on *a*, *c* on *b*, *d* on *c*, &c., along the length of the arrow *B*. This property of the assemblage of spheres is in harmony with the fact that in crystals of the compounds under consideration gliding occurs on the dodecahedron (110), the direction of translation being either 001 or $1\bar{1}0$; these directions are those of the arrows *A* and *B* in Fig. 29*a* (see Table IV). Johnsen has shown (*Jahrb. Min.*, 1902, 2, 133) that of the cubic halogen salts exhibiting gliding on (110), sodium chloride, potassium chloride and iodide, rubidium chloride, and ammonium iodide show the translation direction $1\bar{1}0$, whilst sodium fluoride and ammonium chloride and bromide have the translation direction 001.

The equilibrium arrangement, after the performance of a translation in either of the two directions indicated, is of the same nature as that disturbed by the movement. It is, however, unlikely that the planes of centres nearest to a plane or stratum of gliding remain unaltered during the process; if, as has been postulated, the equilibrium is one between centres of co-existent attraction and repulsion (Trans., 1906, 89, 1676), the effect of the violence done to the structure at the place where gliding actually occurs must be pictured as extending some distance into the mass. Evidence of the occurrence of this is repeatedly found in the work of Ewing and others (*Phil. Trans.*, 1903, 200, *A*, 241) on the slip in strained metals which leads to a temporary loss of elasticity. It is interesting in this connexion to observe the similarity of spacing obtaining between a pair of consecutive layers of a dodecahedron face (110) (Fig. 3), regarded as a single layer, and a single layer of the octahedron face (111) (Fig. 2). Thus the face of each of the two masses concerned in a shift or slip throughout a plane (110) may be regarded as consisting of two layers, the one forming the ridges and the other bounding the hollows of the corrugated face (110); in the case of a shift in the direction *A* (Fig. 29*a*), it is evident that during the first half of the movement pressure is taken off the deformable spheres forming the inner layer of the two, or the trough of the hollow, and put on to the spheres of the outer layer which forms the ridges. Consequently, the arrangement of the spheres of a double layer will, when the shift is half through, approximate to a plane arrangement resembling that of one layer in the face or plane (111). The dimensions in the direction of the shift will, however, be less than in the case of the latter layer, so that along lines having this direction the spheres will be flattened. The perception of this approximation to the surface arrangement of layers of the face (111) renders it easier to see how a shift in the direction *A* can take place with but very little opening of the interstices between the deformable spheres.

It has now been shown that the somewhat complex crystalline properties of the binary compounds of Table IV are in entire harmony with the representative homogeneous assemblage derived from the closest-packed cubic arrangement of equal spheres; it will be shown below that assemblages can also be devised which are similarly representative of the ammonium salts named in the table. It is not suggested that the arrangement of the spheres to form tetrahedral groups as above described indicates polymerisation of the chemical molecules having simple compositions such as KCl. It should, indeed, perhaps be pointed out that the partitioning into tetrahedral groups is a mere geometrical device, useful in elucidating the configuration of the several structures, and that the actual existence of a subdivision of the assemblage of the nature indicated by such a partitioning is not suggested.

The Tri-halogen Compounds of the Alkali Metals.

The study of the tri-halogen compounds of the alkali metals of the type of cæsium tri-iodide, CsI_3, offers a variety of problems of importance, especially in view of the uncertainty which prevails as to their chemical nature. In accordance with our method of formulation, these substances should be regarded as composed of elements of the same fundamental valency, represented therefore by spheres of atomic influence of approximately the same size. Further, since the assemblages representing these substances are built up of almost equal spheres of two or more kinds, they may be expected to conform to the fourth geometrical property, in which case their marshalling will be that of either the cubic or the hexagonal closest-packed assemblage of equal spheres; their axial ratios will in this case approximate to those of one or other of these two assemblages. Most of these compounds, which were crystallographically examined by Penfield (*Amer. J. Sci.*, 1894, **47**, 463; 1893, **43**, 19 and 478), are orthorhombic, but one, cæsium dichloroiodide, is dimorphous, and another, potassium dichloroiodide, is monosymmetric; the data for all the orthorhombic members of the class which have been crystallographically examined are given in Table V together with their equivalence parameters calculated as previously indicated (Trans., 1906, **89**, 1681), the value of *W* being taken as 4.*

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* We may here note that we have never underrated the importance of the study of topic axial ratios for many crystallographic purposes; in the hands of Tutton and others the topic parameters have led to a considerable extension of our knowledge

It will now be established that assemblages appropriate to the constants of the tri-halogen compounds in question can be derived by the superposition of a single kind of triangularly arranged layer such as occurs in the cubic assemblages of the mono-halogen salts of the alkali metals (Fig. 19); in such a layer, spheres representing the halogen and the metal occur in the proportion of 3 : 1 respectively. The former are marked lightly and the latter heavily in Figs. 19*b*, *d*, and *f*. Axial ratios not far removed from those of the orthorhombic compounds of Table V are obtained directly from the three least translations of an assemblage composed of layers, like those of Fig. 19*b*, superimposed in accordance with the mode of packing in the hexagonal closest-packed assemblage. This mode of packing is depicted in Fig. 5, and leads in the present case to the arrangement shown in Fig. 28; in such an assemblage the three axial directions can be chosen at right angles, and the axial ratios, stated in the orthorhombic manner, have the values derived for the hexagonal closest-packed assemblage (p. 1157) of equal spheres, namely $a:b:c = 1 : 2\sqrt{\frac{2}{3}} : \sqrt{3} = 0{\cdot}6124 : 1 : 1{\cdot}0608$. These values may be directly compared with the axial ratios of the orthorhombic tri-halogen compounds of the alkali metals, and give the equivalence parameters, $x : y : z = 1{\cdot}1224 : 1{\cdot}8329 : 1{\cdot}9443$; they may be conveniently spoken of as the ideal axial ratios and ideal equivalence parameters.

A comparison of the ideal values with those of the substances noted in Table V reveals a close correspondence and also departures from correspondence of a periodic character in passing from member to member of the series. It may be noted that a change of the halogen atoms in a compound of the series causes less change in the equivalence parameters than does a change of the atom of the alkali metal; this suggests that the spheres of influence of chlorine, bromine, and iodine are nearly of the same size, and differ more in size from that of the metal in any of the compounds than they do among themselves. Neglecting for the moment differences among the several halogen atoms present in certain of the compounds, it will be seen that the arrangement of Fig. 28 will give the highest symmetry and most even distribution of the less numerous spheres of the assemblage, and in the case where all the spheres are of the same size will form a closest-

of isomorphous replacement, but for the prime object which we have in view, namely, the elucidation of molecular constitution—which is intimately related to the crystalline form through the valencies of the constituent atoms—the topic axial ratios are conveniently replaced by the equivalence parameters. For the purpose of obtaining a more complete knowledge of the relation between crystalline form and chemical constitution it will, at some later stage of the present work, become necessary to discuss together the topic and equivalence parameters.

TABLE V.

	a	: b :	c	x	: y :	z
$RbCl_2Br$	0·7146	: 1 :	1·1430	1·2135	: 1·6982 :	1·9410
$CsCl_2Br$	0·7186	: 1 :	1·1237	1·2250	: 1·7047 :	1·9155
$RbBr_2Cl$	0·70	: 1 :	1·1269	1·2026	: 1·7180 :	1·9360
$RbCl_2I$	0·7341	: 1 :	1·1963	1·2169	: 1·6576 :	1·9830
$CsCl_2I$	0·7373	: 1 :	1·1920	1·2219	: 1·6572 :	1·9754
$RbClBrI$	0·7271	: 1 :	1·1745	1·2166	: 1·6733 :	1·9651
$CsClBrI$	0·7230	: 1 :	1·1760	1·2114	: 1·6756 :	1·9705
$RbBr_3$	0·6952	: 1 :	1·1139	1·2017	: 1·7286 :	1·9255
$CsBr_3$	0·6873	: 1 :	1·0581	1·2132	: 1·7652 :	1·8678
KBr_2I	0·7158	: 1 :	1·1691	1·2058	: 1·6845 :	1·9694
$RbBr_2I$	0·7130	: 1 :	1·1640	1·2044	: 1·6892 :	1·9662
$CsBr_2I$	0·7203	: 1 :	1·1667	1·2116	: 1·6821 :	1·9826
$CsBrI_2$	0·6916	: 1 :	1·1419	1·1877	: 1·7173 :	1·9610
RbI_3	0·6858	: 1 :	1·1234	1·1875	: 1·7316 :	1·9452
CsI_3	0·6825	: 1 :	1·1051	1·1901	: 1·7440 :	1·9273
TlI_3	0·6828	: 1 :	1·1217	1·1846	: 1·7350 :	1·9461
Ideal values...........	0·6124	: 1 :	1·0608	1·1224	: 1·8329 :	1·9443

packed assemblage of the hexagonal form; in the assemblage suggested, each of the less numerous spheres is equidistant from six others in the same layer, and the minimum distance between the less numerous spheres of two succeeding layers is the maximum possible.

Suppose now that all the less numerous spheres alter in magnitude uniformly to a slight extent. If they become sensibly smaller than the others, closest-packing will involve considerable distortion of the assemblage, because the more numerous spheres are already in contact, twelve around each of the less numerous, and the cavity at the centre of the group of twelve large spheres can only be diminished appreciably by a considerable distortion of the shell of spheres surrounding it. It must therefore be concluded that any appreciable change in the relative magnitudes, if it is to alter but slightly the form of the assemblage, must consist in a relative increase in size of the less numerous spheres. A distinct indication is thus obtained that in compounds of the present type the sphere of atomic influence of the metal is larger than that of the halogen; adjustment accompanied by but slight distortion, the occurrence of which is indicated by the equivalence parameters of Table V, being only possible in the case of an appreciable difference in magnitude when each isolated or metallic sphere of influence is surrounded by twelve of a rather smaller size.

In the ideal assemblage the spheres are found in contact along lines having the direction of the axis a. An increase of dimension occurring along this axis alone has a greater proportional effect in enlarging the corresponding axial length than in increasing the total volume, and therefore a difference in magnitude between the two kinds of spheres, those of the halogen and of the metal, has the effect of lengthening the axis a as compared with the other two axes provided that the centres of a layer remain in the same plane. In other words, when the difference in size of the two kinds of spheres is a maximum, x will have the maximum value. It is therefore concluded that the difference between the relative sizes of the spheres of the metal and the halogen is a maximum when x is a maximum and that the value of x will always be greater than the corresponding value for the closest-packed assemblage of equal spheres. Reference to Table V shows that x never diminishes to so small a value as the ideal one of 1·1224; this limiting value is approached most nearly in rubidium and thallium tri-iodides.

When hard spheres are employed, it is evident that any increase in the size of the cavities found between the spheres of a layer tends to shorten the distances between the layers by allowing the spheres of one layer to lie deeper in the cavities of an adjoining layer, and that in no case will this distance be greater than when the spheres of a layer are as closely-packed as possible; consequently, if the suggested condition obtains, y must assume a maximum value in the case of the ideal assemblage. Reference to Table V shows that y never has as large a value as the ideal one of 1·8329.

It is, however, possible to proceed a step further, and, by an extension of the argument just made use of, to indicate the order of relative magnitude of the spheres of atomic influence concerned in the compounds of Table V; when this is done it is found that the results are consistent throughout the series and have some bearing on chemical facts not immediately connected with the questions under discussion. For the sake of convenience the x values of members of Table V may be listed as in Table VI.

TABLE VI.

1.	$RbCl_2Br$	1·2135	$CsCl_2Br$	1·2250
2.	$RbCl_2I$	1·2169	$CsCl_2I$	1·2219
3.	$RbBr_3$	1·2017	$CsBr_3$	1·2132
4.	$RbBr_2I$	1·2044	$CsBr_2I$	1·2114
5.	RbI_3	1·1875	CsI_3	1·1901
6.	$RbBr_3$	1·2017	RbI_3	1·1875
7.	$CsBr_3$	1·2132	CsI_3	1·1901
8.	$CsBr_3$	1·2132	$CsBrI_2$	1·1877
9.	$RbBr_2I$	1·2044	RbI_3	1·1875
10.	$RbCl_2Br$	1·2135	$RbBr_2Cl$	1·2026
11.	$RbCl_2I$	1·2169	$RbBr_2I$	1·2044
12.	$CsCl_2I$	1·2219	$CsBr_2I$	1·2116
13.	$RbCl_2I$	1·2169	RbI_3	1·1875
14.	KBr_2I	1·2058	$RbBr_2I$	1·2044

In connexion with the pairs numbered 1 to 5 it is noted that the x value stated for the first member of each pair is less than that of the second, so that these cases unitedly indicate that the difference between the volumes of the spheres of atomic influence of rubidium and the halogens is less than that for cæsium and the same halogens; consequently, relative to the other constituent spheres, that of rubidium is smaller than that of cæsium. The pair of compounds, RbClBrI and CsClBrI, appears at first sight to furnish an exception to this, the values of x being in the reverse order to the above although differing but slightly. The reason of this may, however, well be that the halogen associated with rubidium on the axis of x is not the same as that associated in a similar manner with cæsium; that is to say, the component complex RbI may correspond with CsCl.

Again, for numbers 6, 7, 8, and 9, the x value of the compound in the first column is greater than the x value in the second column; it is thus indicated that the magnitudes differ more in the former than in the latter and that the volume for bromine is therefore less than that for iodine. For numbers 10, 11 and 12 a similar relation obtains, so that the volume for chlorine is less than that for bromine and consequently also less than that for iodine. The pair numbered 13 also indicates that the volume for chlorine is less than that for iodine. Lastly, the nearly identical x values for the pair numbered 14 indicates that potassium and rubidium possess spheres of influence of nearly identical magnitude. This is strongly confirmed by the axial values for the monosymmetric potassium dichloroiodide, namely, $a:b:c = 0{\cdot}8319:1:0{\cdot}4544$, $\beta = 96°40'$. On stating these axial ratios in the form $b:3c:2a = 1:1{\cdot}3632:1{\cdot}6638$, $\beta = 96°40'$, or $0{\cdot}7336:1:1{\cdot}2205$, $\alpha = 96°40'$, the equivalence parameters $x:y:z = 1{\cdot}2109:1{\cdot}6507:2{\cdot}0147$, $\alpha = 96°40'$ are obtained, and these are almost identical with the values $1{\cdot}2169:1{\cdot}6576:1{\cdot}9830$ for rubidium dichloroiodide, $RbCl_2I$. It is evident that a distortion of an orthorhombic assemblage which changes the interaxial angle β from 90° to 96°40′ would but slightly affect the axial lengths; an independent indication is thus obtained that the spheres of atomic influence of potassium and rubidium are of nearly the same relative volumes.

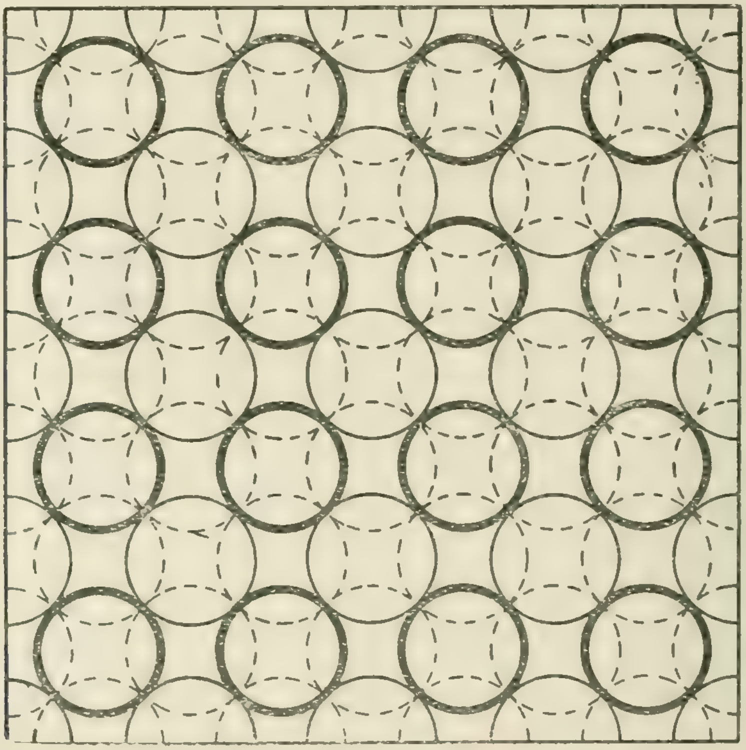
The case of thallic iodide is of particular interest because thallous halogen salts are isomorphous with the corresponding potassium salts, whilst, as is seen from Table V, thallic iodide exhibits axial ratios and equivalence parameters which are identical within the limits of experimental error with those of rubidium tri-iodide. Thallic iodide is therefore a compound of constitutionally identical type with the tri-halogen compounds of the alkali metals and, in the thallic condition, the sphere of atomic influence of thallium has almost precisely the same volume as that of rubidium. The latter conclusion is of some theoretical importance. Tutton has recently (*Proc. Roy. Soc.*, 1907, **79**, *A*, 351) contributed very precise measurements of the orthorhombic crystals of potassium, rubidium, cæsium, and thallous sulphates and selenates, and shows that the geometrical constants of rubidium and thallous sulphates (or selenates) are almost identical, but differ considerably from those of the other alkali salts named. This case is entirely analogous to that of the tri-halogen compounds now under discussion, and shows that in the thallous, as in the thallic, salt the sphere of influence appropriated by thallium is practically identical in volume with that of rubidium. Very substantial corroboration is thus furnished of the correctness of the method which we have adopted for the explanation of multivalency.

In addition to the orthorhombic form noted in Table V, cæsium dichloroiodide, $CsCl_2I$, yields a second crystalline modification which is of trigonal symmetry with $a : c = 1 : 0{\cdot}9636$. This form may be derived from the cubic mode of closest-packing by referring this assemblage to an axial system consisting of the body perpendicular of a tetrahedral group of four spheres, and the three axes at right angles to this in the plane of a triangularly arranged layer; the latter three axes represent the face perpendiculars of the tetrahedral group of four spheres and the former direction is a trigonal axis. The axial ratio thus becomes $a : c = \frac{1}{2}\sqrt{3} : \sqrt{\frac{2}{3}} = 0{\cdot}8660 : 0{\cdot}8165 = 1 : 0{\cdot}9428$. The centres of one-fourth of the spheres in such an assemblage form a cubic space lattice as may be realised by superimposing the three layers, *b*, *d*, and *f*, of Fig. 19; if these spheres represent the spheres of influence of the metallic atoms, the remaining spheres, which represent chlorine and iodine, can be so allotted that the assemblage possesses trigonal holoaxial symmetry, screw trigonal axes traversing the triangularly arranged layers referred to at right angles; digonal axes intersect strings of centres in each layer. Such a disposition of spheres of slightly different magnitudes appropriately related would be expected to produce such a slight lengthening in the direction of the surviving trigonal axis of the original cubic assemblage as is represented by the change from the ideal axial ratio $a : c = 1 : 0{\cdot}9428$ to the observed value of $a : c = 1 : 0{\cdot}9636$.

The case of potassium hydrogen fluoride, KHF_2, may be conveniently referred to here; this substance exhibits tetragonal symmetry with $a : c = 1 : 0{\cdot}6010$ (Senarmont, *Ann. des Mines*, 1857, [v], 11, 301). The cubic closest-packed assemblage of equal spheres can be referred to three rectangular axes consisting of a cube edge and two face diagonals; the axial ratio then becomes $a : c = 1 : 1/\sqrt{2} = 1 : 0{\cdot}7071$. In this assemblage let one-fourth of the spheres, so selected that their centres form a cubic space-lattice, experience a somewhat considerable increase in magnitude; if the alternate layers of square order containing these spheres and lying perpendicular to a four-fold axis, as in Fig. 30, are to retain this order, the system must contract along the direction perpendicular to the planes of these layers in order that close-packing may be established. In this manner a contraction of the structure in the direction of the axis c could be brought about which, in order of magnitude, represents the change from the ideal value $a : c = 1 : 0{\cdot}7071$ to the observed value $a : c = 1 : 0{\cdot}6010$. An indication is thus obtained that the sphere of influence of potassium differs considerably in magnitude from those of hydrogen and fluorine, and that the latter are notably smaller than those of the halogens chlorine, bromine, and iodine.

As a general result of the foregoing discussion the conclusion is drawn, not only that all the compounds dealt with which consist of atoms of the same valency conform to the expectation that their structures are derivable from either the hexagonal or the cubic closest-packed assemblage of equal spheres by the application of the fourth geometrical property, but also that definite conclusions can be drawn as to the relative order of magnitude of the spheres of atomic influence of the univalent elements. It has been seen that the magnitude of the sphere of atomic influence increases progressively throughout the series K to Rb, or Tl to Cs, and F to Cl to Br to I, or that as the series formed by the alkali metals and by the halogens in the periodic table is descended the relative magnitudes of the spheres of atomic influence increase. This result is of general interest as elucidating a somewhat obscure aspect of valency which has not previously been

FIG. 30.



precisely stated. It is an observed fact in connexion with the halogen compounds of elements which exhibit multivalency that, with certain of the halogens, compounds are produced the compositions of which are in agreement with the valency law and with the general observation that the valency of an element changed by two and multiples of two, but with fluorine and sometimes also with chlorine a compound is frequently formed in which the valency of the other element does not follow the rule. Thus sulphur, which is bi- or quadri-valent towards chlorine, bromine, and iodine, yields with fluorine the pentafluoride, SF_5, and other analogous cases might be quoted (Trans., 1906, **89**, 1737). The reason suggested for this is that whilst the sphere of atomic influence of sulphur has approximately twice the volume of that of a univalent atom, this statement expresses its relation to fluorine less accurately than it does its relation to chlorine, bromine, or iodine.

The Penta-halogen Compounds of the Alkali Metals.

Several of the penta-halogen compounds of the alkali metals have been crystallographically examined by Penfield (*Amer. J. Sci.*, 1893, **44**, 46); the axial ratios obtained are as follows:

Cæsium pentaiodide, CsI_5, anorthic, $a : b : c = 0{\cdot}9890 : 1 : 0{\cdot}4276$.

$\alpha = 96°56'$. $\beta = 89°55'30''$. $\gamma = 90°21'30''$.

Potassium tetrachloroiodide, KCl_4I, monosymmetric,

$a : b : c = 0{\cdot}9268 : 1 : 0{\cdot}4472$, $\beta = 95°42'$.

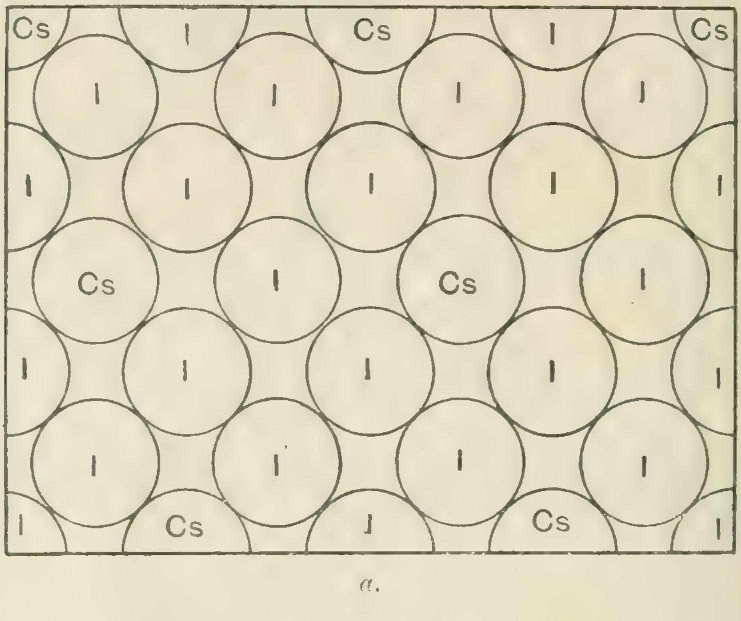
Cæsium tetrachloroiodide, $CsCl_4I$, monosymmetric,

$a : b : c = 0{\cdot}9423 : 1 : 0{\cdot}4277$, $\beta = 93°40'$.

The quantity and the nature of the crystallographic evidence bearing on these substances are not such as to allow of the deduction of such convincing arguments concerning structural configuration as those produced in the case of the alkali trihalides. It will therefore suffice to show that the crystallographic data available for the pentahalides are entirely in harmony with our mode of regarding the constitution of the alkali mono- and tri-halides.

If in a layer parallel to the cube plane (Fig. 4) of the closest-packed cubic assemblage of equal spheres, one sphere in every six differs from the others, the most even distribution of the differing spheres is that shown in Fig. 31. The homogeneity of distribution of the latter is preserved if the projections of any two consecutive layers on the same area are as depicted in Figs. *a* and *b* of Fig. 31; it must, however, be noted that if more than two succeeding layers are considered together, the combined projection does not consist of only the two plans depicted in Fig. 31. In the structure representing cæsium pentaiodide the differing spheres would be those marked Cs in the diagram, whilst the others marked I, which are five times as numerous, represent the iodine atoms. If the sphere of atomic influence of cæsium is larger than that of iodine, as has already been argued (p. 1194), the former spheres could be accommodated by a

FIG. 31.



a.

b.

spreading of the structure in the plane of the cube layers; this spreading will necessarily be accompanied by a shrinking in a direction perpendicular to this plane. The conversion of the closest-packed cubic assemblage of equal spheres into that depicted in Figs. 31, *a* and *b*, should result in the latter becoming, in accordance with the fourth geometrical property, a pseudo-cubic assemblage in which one axial direction differs essentially in kind from the other two. In the cases of the three substances under consideration this seems indicated by the crystal growth or habit occurring in such a way that unit length on the axis c is conveniently stated as rather less than one-half the corresponding value for the axis a, whilst unit length on the axes a and b are nearly the same. In the three pentahalides the ratio $a:b$ is slightly greater than unity, whilst that of $b:2c$ is, in accordance with the foregoing, slightly less than unity.

Layers such as are depicted in Fig. 31 do not pack very symmetrically on one another, but a very even distribution of the two kinds of sphere making up the assemblage CsI_5 is obtained if the two figures 31, a and b, represent the projections upon the same area of any two succeeding layers. This kind of symmetry of distribution of two kinds of spheres has, however, holohedral anorthic symmetry, and, the symmetry of arrangement being anorthic and the two kinds of spheres differing slightly in size, the slight adjustments of the assemblage which lead to close-packing in pseudo-cubic symmetry will also necessarily be anorthically symmetrical. The slight departure of the axial directions from perpendicularity, represented by the divergence of the interaxial angles α, β, and γ from 90°, thus finds a natural explanation.

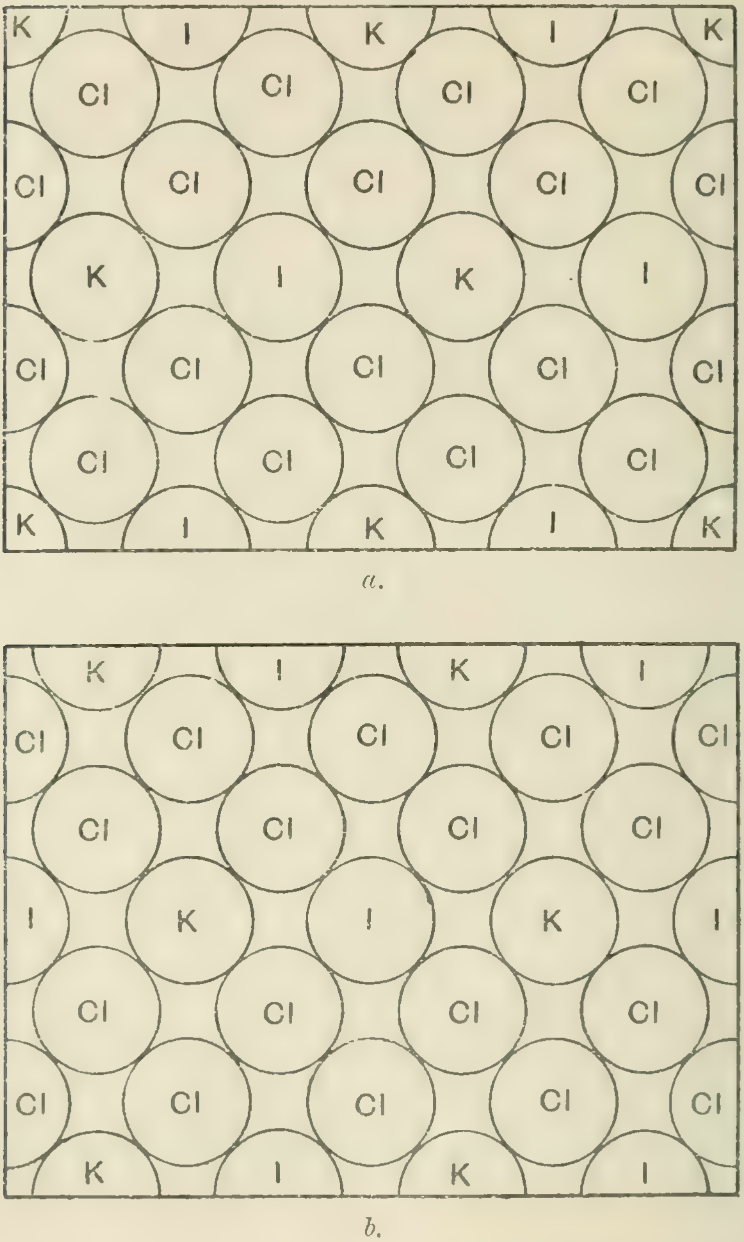
It is perhaps significant that cæsium pentaiodide, CsI_5, exhibits anorthic symmetry, whilst cæsium tetrachloriodide, $CsCl_4I$, and potassium tetrachloroiodide, KCl_4I, which are constitutionally less symmetrical, crystallise in a morphotropically related form belonging to the more highly symmetrical monosymmetric system. This would appear to be due to the arrangement as compared with that in the cube layers shown for CsI_5 in Fig. 31 being, in the case of the tetrachloroiodides, of the more symmetrical kind depicted in Fig. 32; Figs. 32, a and b, represent the projections upon the same area of any two successive layers in the structure of potassium or cæsium tetrachloroiodide. The translations are of approximately the same magnitude as in the preceding case, but the symmetry of arrangement of the component spheres is now monosymmetric; the adjustments of the structure which lead to close-packing are therefore also possessed of monosymmetric symmetry.

Potassium Silver Iodide, K_2AgI_3.

The following double salts crystallise in the orthorhombic system (Penfield, *Amer. J. Sci.*, 1892, [iii], 44, 157) and, since the constituent elements are all univalent, the assemblage appropriate to each salt must be regarded as built up from spheres of approximately the same size, as in the cases previously considered.

2KI,AgI $a : b : c$ = 0·977 : 1 : 0·234.
2RbI,AgI ,, = 0·977 : 1 : 0·236.
2CsCl,AgCl ,, = 0·971 : 1 : 0·244.

Fig. 32.

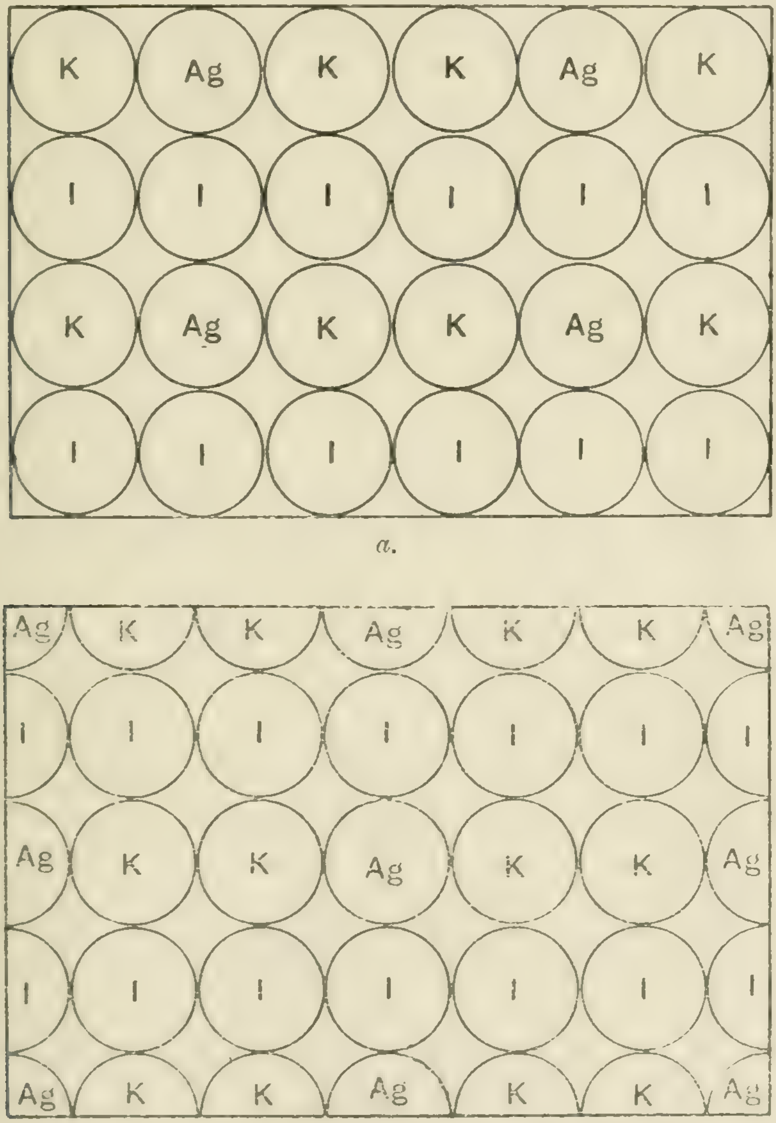


a.

b.

On distributing equal spheres lying in the cube planes of the cubic closest-packed assemblage of equal spheres in the manner indicated in Fig. 33, *a* and *b*, each of these representing the projection on the same area of alternate planes of spheres, an arrangement possessing orthorhombic symmetry is obtained. The directions of the rectangular axes of the assemblage are those of the translations in the plane of the diagrams and the translation perpendicular thereto, and selecting appropriate units, the axial ratios $a:b:c=3:3:1/\sqrt{2}=1:1:0{\cdot}235$ are obtained. These values are sufficiently near approximations to the observed values noted above to permit of the supposition that the assemblage appropriate to these salts is a pseudocubic one derived by means of the fourth geometrical property from the cubic closest-packed assemblage of equal spheres. The evidence is not, however, adequate to establish that the arrangement indicated is that which actually obtains.

FIG. 33.



a.

b.

The Ammonium Halogen Salts.

The close-packed, homogeneous assemblage representing ammonium chloride may be regarded as derived from that of potassium chloride by aid of the first and second geometrical properties of such assemblages built up from deformable spheres. These geometrical properties may be conveniently stated in the following manner with somewhat greater precision than before (Trans., 1906, 89, 1730).

First Property.—Let homogeneously situated spheres, each of volume m, be removed from a homogeneous, close-packed assemblage of deformable spheres, and let the similar vacant spaces disclosed be reoccupied each by a similar group consisting of two or more spheres having the total volume m; then if the shape of the cavities can, without remarshalling the assemblage, be adapted to the shape of the introduced groups by some mere distortion and local adjustment, the close-packing is found to be preserved.

Two assemblages related in the manner just described, namely, the original and the derived assemblages, have certain portions of their units of partitioning alike; in other words, they contain similar radicles and these have the same marshalling in both assemblages.

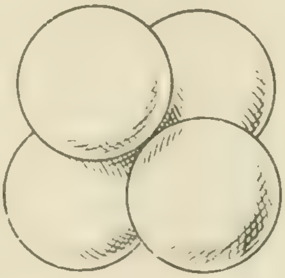
Second Property.—If the molecular units of two homogeneous assemblages of deformable spheres, which are about equally closely-packed, are partially similar in composition and the similar parts have the same marshalling in both, whilst the dissimilar parts are of different valency volumes, the amount of the difference will be two volumes or a simple multiple, 2, 3, or 4, of two volumes of the sphere of influence of minimum magnitude, namely, that corresponding to valency 1, for every molecular unit.

In connexion with these geometrical properties, no assertion is made as to the amount of distortion which can take place without involving remarshalling; probably among those assemblages, whose structure is very simple, cases can arise in which the geometrical possibilities of this kind are more or less narrowly limited. If, however, a substitution is possible which can be accompanied by a distortion that restores the close-packing, the relation between the substituted and substituting spheres will be found to be that expressed by one or other of the geometrical properties stated. In every case the assemblages for which these properties hold must be built up of deformable spheres and be subject to a general pressure sufficient practically to eliminate the interstices as already described.

The assemblage appropriate to ammonium chloride may be derived from that of potassium chloride with the aid of the second geometrical property, by replacing each potassium sphere of volume 1 by a group of volume 4 composed of a nitrogen and a hydrogen sphere; the property then demands the insertion of three more hydrogen spheres in order that close-packing may occur without remarshalling.

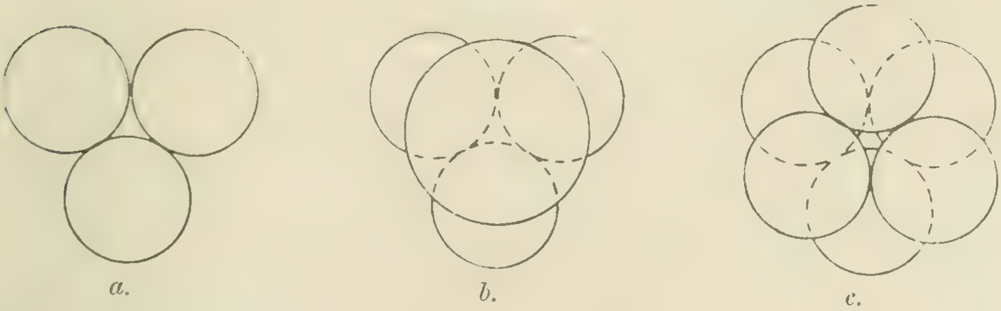
The same assemblage for ammonium chloride can be reached by aid of the first geometrical property alone in the following manner. Construct an assemblage similar to the holohedral cubic closest-packed assemblage of two kinds of spheres from which the potassium chloride assemblage was derived, but in which the component spheres are of volume 4 instead of volume 1; then replace each sphere of the one set by two spheres of volumes 1 and 3 respectively, so that the tetrahedral groups of four spheres each of volume 4 in the set become substituted by the groups 4(NH), packing as closely as possible without remarshalling the assemblage. Finally, replace each sphere of the other set by four spheres of volume 1, three of these representing hydrogen and one representing chlorine. The plasticity of groups consisting of several small spheres fitted together obviously renders it easier to adapt the shape of the inserted complex to that of the cavity which has to receive it.

FIG. 34.



The identity in crystalline function exhibited by corresponding potassium and ammonium compounds indicates an extremely close resemblance in marshalling, and, guided by the theoretical considerations just put forward, a form and an arrangement for complexes of the compositions 4(NH) and $4ClH_3$ have been determined of such a nature that the complex tetrahedral groups occupy situations and display geometrical properties closely analogous to those of the tetrahedral groups of the simpler assemblage.

FIG. 35.

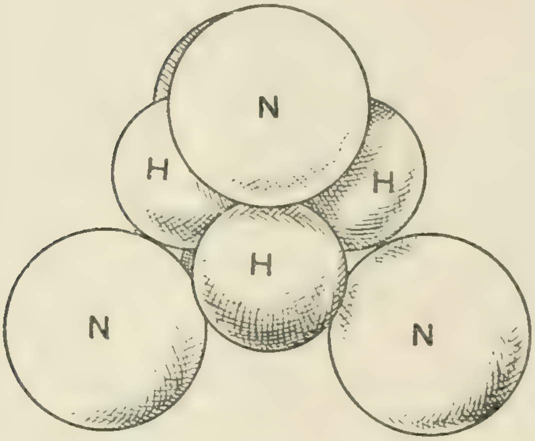


A group of the composition 4(NH) tetrahedrally arranged is formed from a tetrahedral group of the composition 4H (Fig. 34) by placing in each of the four hollows found on the faces of the latter (Fig. 35*a*) a sphere of the volume 3 (Fig. 35*b*); the composite tetrahedral group thus obtained has the appearance shown in Fig. 36.

A number of these groups are so placed that their centres occupy the centres of half the cubes of a cubic partitioning of space symmetrically selected as in the case of silver iodide and potassium chloride. The groups are similarly orientated in accordance with cubic symmetry, and the scale of the partitioning is such that half the total space is allotted to these groups; this has the effect of so spacing them that they are in contact at their corners without any considerable distortion. The spheres of volume 3 are then found to form close tetrahedral groups, the centres of which occupy half the cube angles of the partitioning, these latter being symmetrically selected by the process of derivation indicated. The skeleton assemblage formed in this way then resembles that formed by one set of spheres of the potassium chloride assemblage in the following respects:

(*a*) The centres of the composite tetrahedral complexes lie at the centres of half the cubes, symmetrically selected as indicated in Fig. 17, of a cubic partitioning of space of appropriate dimensions.

FIG. 36.



(*b*) The apices of adjoining tetrahedral complexes, in this case the spheres of volume 3, are associated in fours to form complexes of tetrahedral shape the centres of which lie at half the cube angles of the partitioning, these being symmetrically situated.

(*c*) The assemblage displays cubic symmetry.

(*d*) Neglecting small interstices, the constituent spheres of the skeleton assemblage, when deformable spheres are used, occupy one-half the total space.

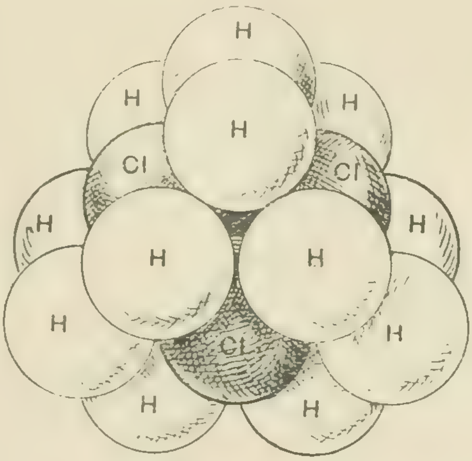
(*e*) The assemblage possesses geometrical properties corresponding with the observed facts as to twinning, cleavage, and gliding; these properties and facts in the case of the ammonium halogen salts are analogous to those relating to the simpler halogen salts of the alkali metals.

The two compared skeleton assemblages, namely, those composed of the groups 4K and 4(NH) repectively, differ in that the simpler one possesses centres of symmetry at the centres of the spheres and also digonal axes passing through those centres, so that the crystal system is the holohedral cubic, whilst the derived assemblage 4(NH) possesses neither centres nor tetragonal axes of symmetry, so that its crystal symmetry is the tetrahedral cubic.

Since, when deformable spheres are used, the cavities present in the assemblage 4(NH), like those in the simpler skeleton assemblage 4K, comprise as much space as that occupied by the constituent spheres, the spaces between the complexes 4(NH) will, if the packing is close, suffice to accommodate complexes of the composition 4(3H + Cl), as both kinds of complex have the valency volume 16. As the cavities have a tetrahedral shape, the complexes 4(3H + Cl) must be of a tetrahedral form resembling that of the simpler complex 4Cl; a form of this nature is obtained as follows.

Upon each of the four faces (Fig. 35*a*) of a close tetrahedral group of four spheres of volume 1 (Fig. 34), representing 4Cl, is placed a triad of three hydrogen spheres oppositely orientated to the triad 3Cl composing the face as indicated in Fig 35*c*. A composite tetrahedral group of the composition 4(3H + Cl) is thus obtained; its valency volume is 16, and its appearance is shown in Fig. 37.

FIG. 37.



Although the cubic partitioning of space in this case accommodates the groups 4(NH) and 4(3H + Cl) respectively, instead of, as in the former case, the groups 4K and 4Cl, it must be remembered that this is a mere geometrical device and does not necessarily indicate any attachment of the atoms to form a molecular aggregate.

In the potassium chloride assemblage before its final adjustment, four different sets of highly symmetrical points may be discerned, namely, two sets of cube centres of the partitioning, distinguished by being occupied by the centres of the two kinds of tetrahedral groups, 4K and 4Cl, which have the same orientation, and the two sets of cube corners similarly distinguished, and the grouping about which is of opposite orientation to that about the cube centres. These four kinds of points lie on the trigonal axes, as present before their number is diminished to one-fourth by the adjustment, and may be respectively distinguished by the letters *A*, *B*, *C*, and *D*. *A* is a cube corner, *B* a cube centre, *C* a cube corner, and *D* a cube centre; these different kinds of points lie equidistant along any trigonal axis in the order *A*, *B*, *C*, *D*, *A*, *B*, &c., and, in the case of the simple assemblage, each of the points is the centre of a tetrahedral group; every sphere in the assemblage participates in two of the groups whose centres are alphabetically distinguished consecutively.

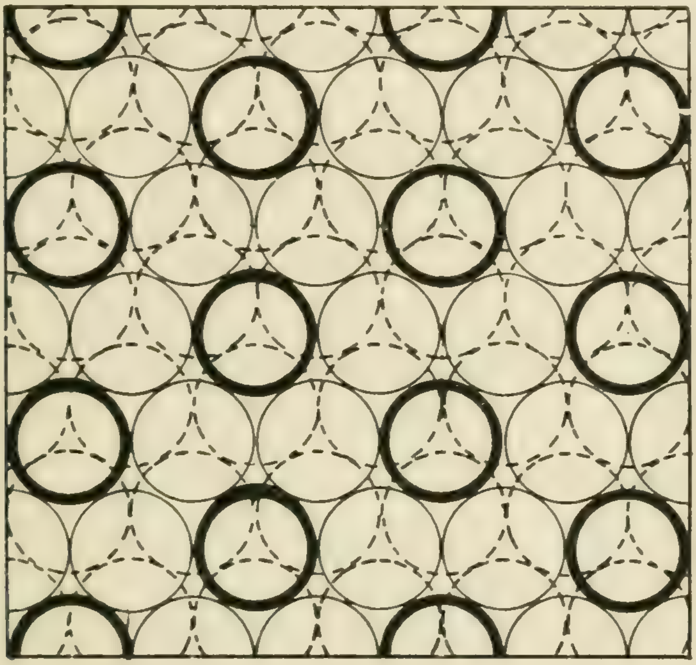
If in the corresponding ammonium chloride assemblage a similar lettering is employed, the centres of the tetrahedral groups $4(NH)$ will occupy one set of centres, as A, and the centres of the tetrahedral group $4(3H + Cl)$ the centres next but one to them on the trigonal axis, as C. The vertices N of adjoining $4(NH)$ complexes are, as has been pointed out, associated in fours to form tetrahedral groups $4N$, and these are centred at either B or D according to the order of the lettering with respect to the orientation of the groups. Tetrahedrally arranged groups of the composition $12H$ or $4 \times 3H$ are similarly centred around the remaining centres, D or B, by a similar combination of the vertices of the groups $4(3H + Cl)$. A difficulty apparently arises in connexion with the formation of the last named groups because twelve spheres similarly disposed about a centre as closely as possible leave some considerable space unoccupied at the centre itself, and this is inconsistent with maximum closeness of packing. This difficulty disappears when an adjustment corresponding to the adjustment described in the simpler case of potassium chloride is made, for in this event the only element of symmetry of the 12-point cluster in question, the survival of which is requisite in order that the assemblage may retain a symmetry belonging to the cubic system, is a trigonal axis through the centre of the cluster; the shell of twelve spheres may therefore be distorted so as to become close-packed without necessitating degradation of the symmetry below that of some class of the cubic system.

Previous to this adjustment, which is necessary for the establishment of close-packing, the assemblage displays crystallographical symmetry of the tetrahedral cubic class, namely, Class 31 of Groth; the degradation of type, consequent on local rotation of part of the structure, leads to the loss of the planes of symmetry and therefore to the passage of the assemblage to tetartohedral symmetry of the cubic system.

The display by the crystals of ammonium chloride of gyrohedral hemihedrism is to be attributed to twinning of kinds resembling the two species of twinning described in the case of potassium chloride, which do not lead to an increase of the number of faces in the case of that gyrohedrally hemihedral structure. In the case of the tetartohedral structure which has been attributed above to ammonium chloride, however, this kind of twinning doubles the number of faces exhibited by the hexakisoctahedron or general form, and, if equally prevalent in each direction in which it can occur, should reveal itself by raising the symmetry to that of the gyrohedral hemihedrism of the cubic system. If more or less prevalent in one equivalent direction than in another it should give rise to a modification of crystal symmetry such as parallels the modification of crystal symmetry known to occur with the ammonium halogen salts, and which results in the preferential growth of the crystal in the direction of a trigonal or tetragonal axis of cubic symmetry.

It has been argued above that the ammonium chloride assemblage may be regarded as derived from that of potassium chloride by arranging the two sets of composite tetrahedral groups, 4(NH) and 4(3H + Cl), which have the same valency volume, in the same manner as the two sets of simpler tetrahedral groups, 4K and 4Cl, were arranged. If this is so, a mode of twinning and a set of gliding planes can be devised for the more complex assemblage of precisely the same nature as that described in the case of the simpler one.

FIG. 38.

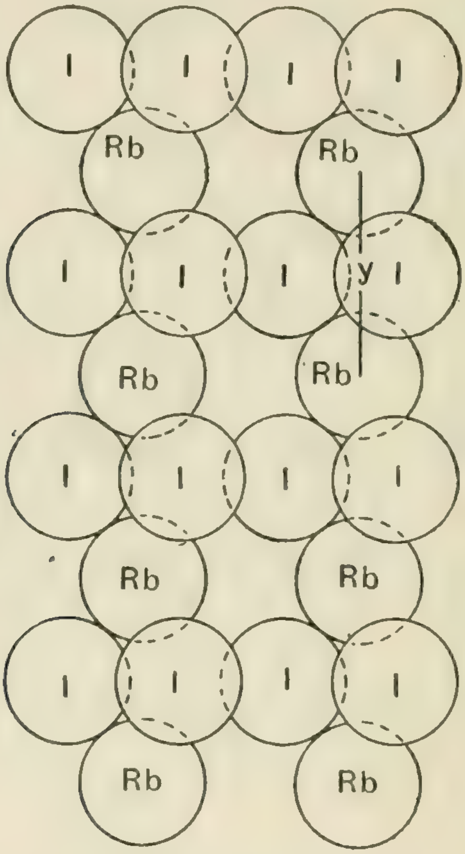


Ammonium Tri-iodide.

Ammonium tri-iodide, NH_4I_3, crystallises in the orthorhombic system with the axial ratios $a:b:c = 0·6950:1:1·1415$ (Penfield, *loc. cit.*); these values differ but little from those quoted above for rubidium tri-iodide and are almost identical with those for cæsium di-iodobromide. The assemblage appropriate to ammonium tri-iodide may be regarded as derived from that of crystalline rubidium tri-iodide by substituting each rubidium atom or sphere of valency or volume 1 by the group NH of valency volume 4 and re-establishing close-packing without remarshalling by the simultaneous insertion of three hydrogen spheres in accordance with the second geometrical property. It is, however, slightly more simple to derive the required assemblage from that of the hypothetical compound, RbI, 2HI, also with the aid of the second geometrical property.

A close-packed homogeneous assemblage representing the compound H_2RbI_3, in which the component spheres of atomic influence are of approximately the same size, may be built up so as to have the marshalling of the hexagonal closest-packed assemblage of equal spheres. In view of the approximate equality in size of the component spheres, it can differ from the latter assemblage mainly in symmetry; it may be regarded as composed of two kinds of layers of the compositions H_2Rb and I_3, layers of the same kind having the same projection on the plane of the layer. The ideal assemblage composed of equal spheres is depicted in plan in Fig. 38, in which the projections of the spheres representing Rb, H, and I are distinguished by circles drawn in heavy, light, and dotted lines respectively.

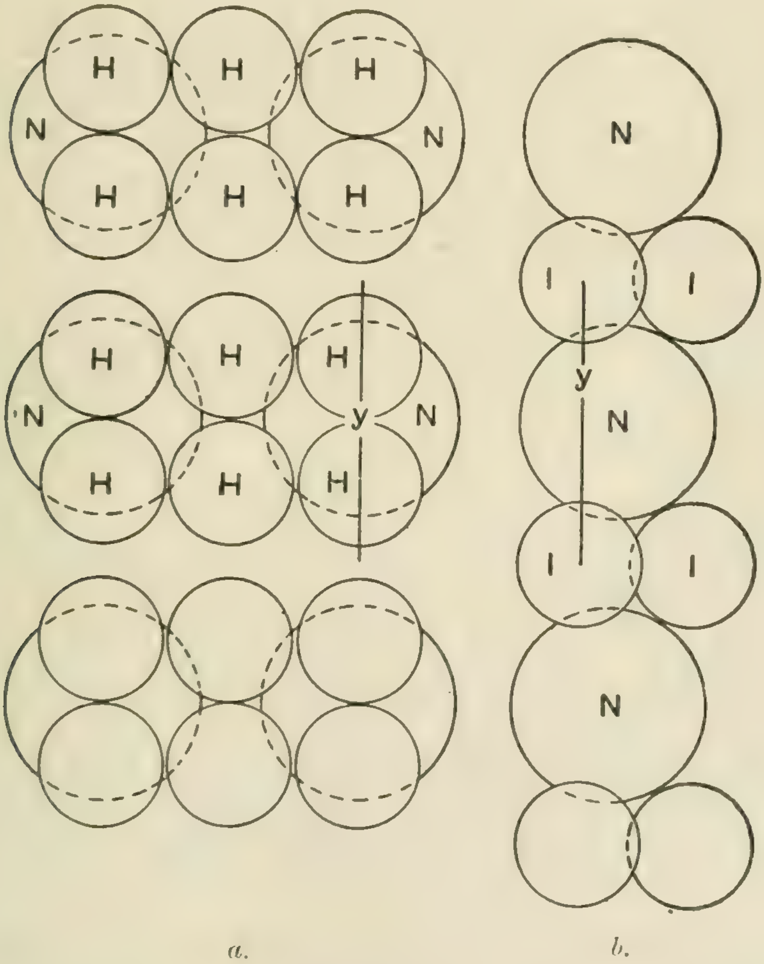
FIG. 39.



This assemblage may be regarded as derived from that of either NH_4Cl, RbI, or RbI_3, by application of the second geometrical property or from that of RbI_5 by means of the first geometrical property. It is composed of strings of spheres in contact, in which single Rb spheres alternate with similarly orientated triads of spheres, I_3; the elevations of these are shown in Fig. 39, two hydrogen spheres being in addition attached to each Rb sphere.

When a number of the figured strings of spheres, RbI_3, are packed together as in Fig. 39, cavities are left which just suffice for the accommodation of the proportion, 2H, of hydrogen spheres; by this addition, the assemblage H_2RbI_3 of Fig. 38 is obtained. The Rb spheres of volume 1 may now be replaced by N spheres of volume 3 so as to give strings of spheres of the composition NI_3 as shown in Fig. 40*b*; the plan of the packed skeleton assemblage NI_3 is shown in Fig. 41. But in this assemblage are left, in accordance with the second geometrical property, cavities sufficient to accommodate a further proportion of two hydrogen spheres for each nitrogen sphere introduced; the replacement of Rb by N naturally involves the spreading of the assemblage in all directions, and for each component I_3 of the one layer there is now present the radicle NH_4 in adjoining layers.

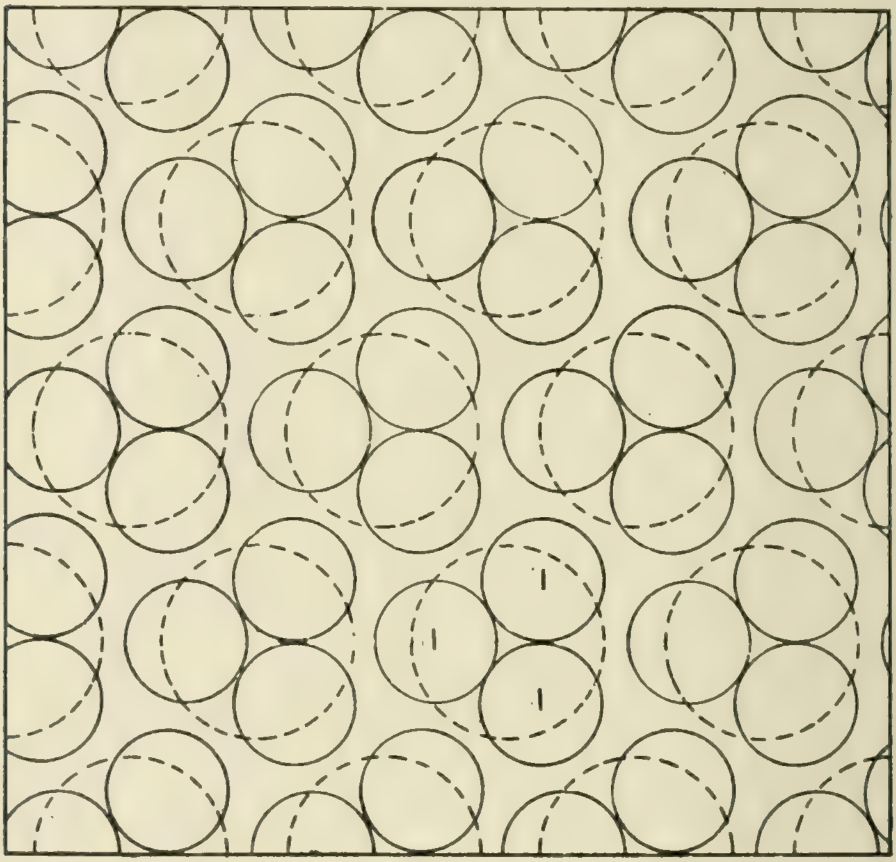
FIG. 40.



a. *b.*

The hydrogen spheres are present in the assemblage in situations indicated in the elevation of a layer given in Fig. 40*a* and in the plan of the assemblage shown in Fig. 42; these represent the arrangement of the composite stratum of the composition, NH_4, consisting of a central layer of N spheres, closely sandwiched between two layers each of the composition 2H. The spheres of the one hydrogen layer make contact with those of the other similar layer in the plane containing the centres of the N spheres, and both hydrogen layers have the same projection. Fig. 43 represents the elevation of the complete assemblage produced by intercalating Figs. 40*a* and 40*b*; the N and I spheres are represented as dotted circles and the H spheres as continuous circles.

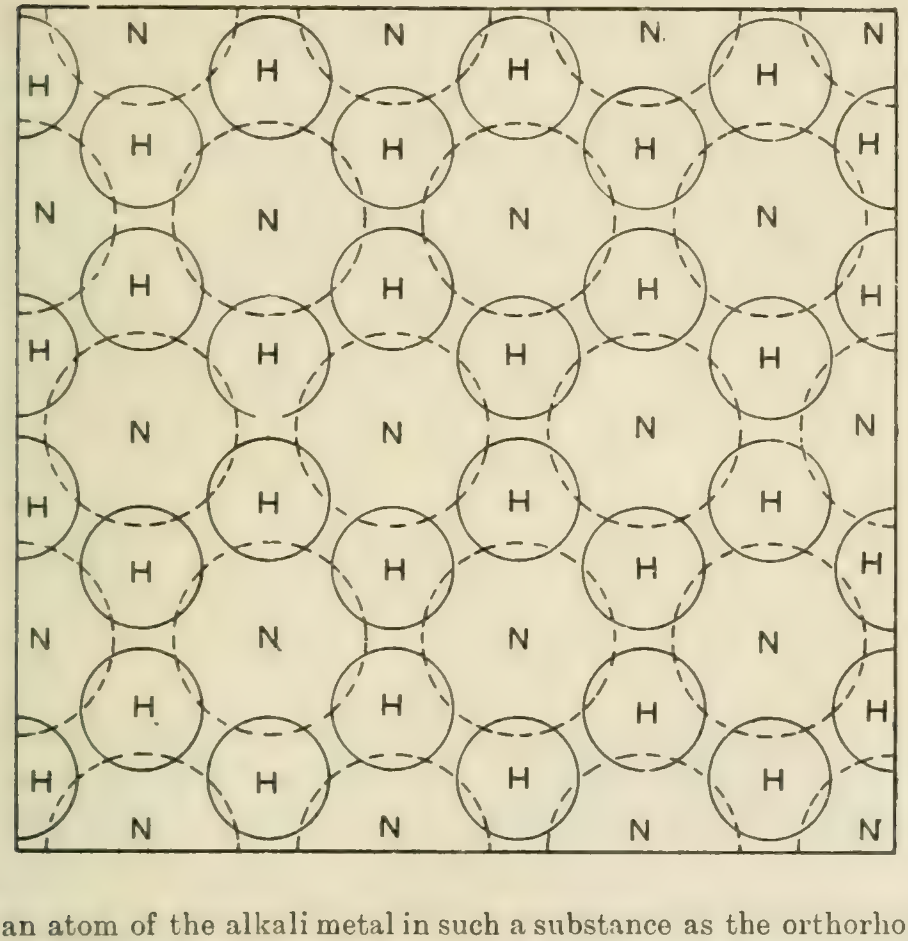
FIG. 41.



The valency volumes of NH_4I_3 and RbI_3 are in the ratio of ten to four and, since there is isomorphism, the equivalence parameters of the two substances should therefore be in the ratio of $\sqrt[3]{10}$ to $\sqrt[3]{4}$; the corresponding translations of the two assemblages are approximately in this ratio, and one of the three, namely, *y*, is indicated in the diagrams. In each case the ratios of the equivalence parameters *x*, *y*, and *z* should be approximately the same as for the closest-packed hexagonal assemblage of equal spheres, and the observed divergences must be attributed, as in previous cases, to slight distortion of the assemblages traceable to small incompatibilities between the sizes of the component spheres of atomic influence. The distortion, as in previous cases, leads to an expansion of the assemblage in the plane of one layer which is compensated for by a corresponding contraction of the dimensions of the assemblage in a plane perpendicular thereto.

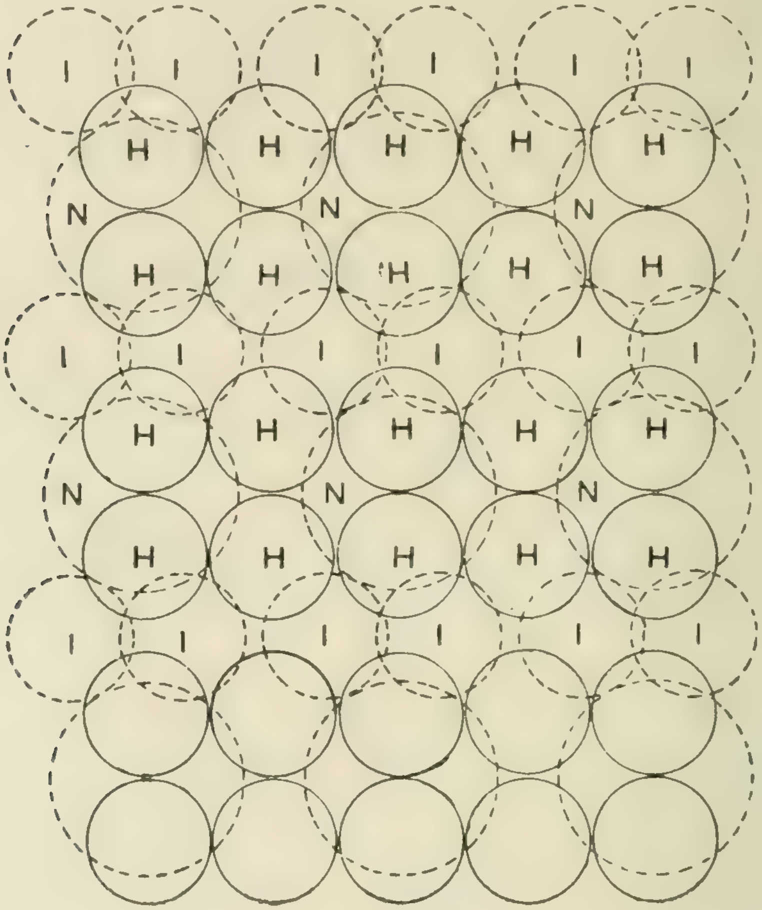
It is interesting to notice that the substitution of the group NH_4 for an atom of the alkali metal in such a substance as the orthorhombic rubidium tri-iodide, in accordance with the second geometrical property, leads to a similar alteration of the dimensions of the assemblage in the three crystallographically principal directions (compare also Tutton, Trans., 1905, 87, 1123). The same kind of result has been shown to occur in the passage from the assemblage representative of the cubic potassium chloride to that of ammonium chloride. The detailed discussion of these two examples in the foregoing pages furnishes a severe test of the applicability of the second geometrical property and affords an explanation of the generally observed

FIG. 42.



isomorphous replacement of potassium, rubidium, or cæsium by the ammonium radicle.

FIG. 43.



The authors' thanks are again due to the Committee of the Municipal School of Technology for permitting the blocks illustrating the paper to be made in the school, and to Messrs. Chas. W. Gamble and R. B. Fishenden, of the Photographic and Printing Crafts Department, for the care with which they have executed the work.

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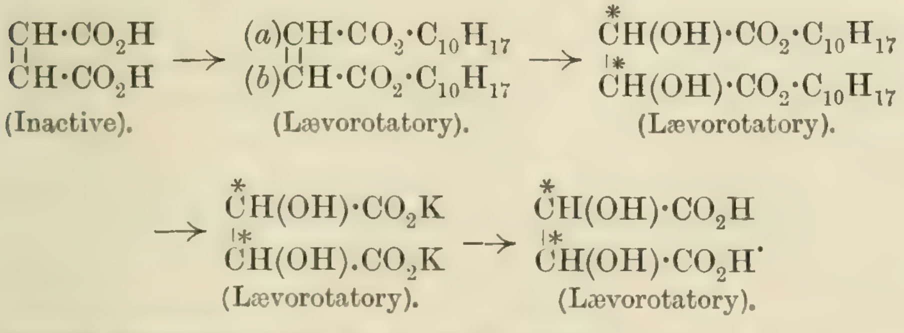
CXII.—*Studies in Asymmetric Synthesis. VI. The Asymmetric Synthesis of the Optically Active Tartaric Acids.*

By ALEX. MCKENZIE and HENRY WREN.

IN 1879, Tanatar (*Ber.*, **12**, 2293) found that fumaric acid or an alkaline fumarate is oxidised in the cold by potassium permanganate to give, in addition to small quantities of oxalic acid and carbon dioxide, an acid, to which the formula $C_4H_4O_6$ was assigned, and which was designated as "Bioxyfumarsäure." Kekulé and Anschütz were, however, struck by the close resemblance which this acid of Tanatar bore to ordinary racemic acid in the general behaviour both of itself and of its salts, and those authors, on repeating Tanatar's work, came to the conclusion that the acid in question is none other than racemic acid (*Ber.*, 1880, **13**, 2150). Further experiments by Anschütz (*Annalen*, 1884, **226**, 191) confirmed this view.

The asymmetric synthesis of the optically active tartaric acids recorded in the present paper was rendered possible by the observations referred to. *l*-Tartaric acid may be asymmetrically generated by means of *l*-borneol in accordance with the scheme:



$$\begin{array}{c}\mathrm{CH\cdot CO_2H}\\ \|\\ \mathrm{CH\cdot CO_2H}\\ \text{(Inactive).}\end{array} \longrightarrow \begin{array}{c}(a)\mathrm{CH\cdot CO_2\cdot C_{10}H_{17}}\\ \|\\ (b)\mathrm{CH\cdot CO_2\cdot C_{10}H_{17}}\\ \text{(Lævorotatory).}\end{array} \longrightarrow \begin{array}{c}\overset{*}{\mathrm{C}}\mathrm{H(OH)\cdot CO_2\cdot C_{10}H_{17}}\\ |\\ \overset{*}{\mathrm{C}}\mathrm{H(OH)\cdot CO_2\cdot C_{10}H_{17}}\\ \text{(Lævorotatory).}\end{array}$$

$$\longrightarrow \begin{array}{c}\overset{*}{\mathrm{C}}\mathrm{H(OH)\cdot CO_2K}\\ |\\ \overset{*}{\mathrm{C}}\mathrm{H(OH).CO_2K}\\ \text{(Lævorotatory).}\end{array} \longrightarrow \begin{array}{c}\overset{*}{\mathrm{C}}\mathrm{H(OH)\cdot CO_2H}\\ |\\ \overset{*}{\mathrm{C}}\mathrm{H(OH)\cdot CO_2H}\\ \text{(Lævorotatory).}\end{array}$$

l-Bornyl fumarate owes its optical activity solely to the presence of the *l*-bornyl group. When a solution of this compound in glacial acetic acid is oxidised by potassium permanganate, the two carbon atoms (*a*) and (*b*) become asymmetric under the influence of the active bornyl group. A mixture of unequal amounts of *l*-bornyl *d*-tartrate and *l*-bornyl *l*-tartrate, containing a very slight excess of the latter, is produced. When this mixture is saponified by an excess of potassium hydroxide and the resulting borneol completely removed, the aqueous solution of potassium salt obtained is lævorotatory. This activity is due to the presence in the aqueous solution of a mixture of potassium *d*- and *l*-tartrates, containing the latter in very slight excess.

Minguin (*Compt. rend.*, 1905, **140**, 946) had previously described the preparation of *l*-bornyl fumarate from fumaric acid and *l*-borneol. He gives the melting point as 102—105°; that obtained by us was 106°. Minguin states that 0·392 gram of ester in 25 c.c. of alcohol gave $\alpha - 1° \ 42'$ in a 20-cm. tube. If we assume that Minguin dissolved 0·392 gram of ester in ethyl alcohol and then made up the solutions to 25 c.c. with ethyl alcohol, then:

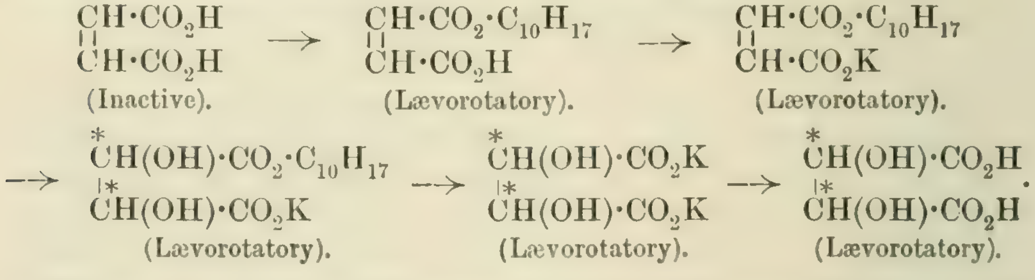
$$l = 2,\ c = 1{\cdot}568,\ \alpha_D - 1{\cdot}70°,\ [\alpha]_D - 54{\cdot}2°.$$

We find that the ester has the following rotation in ethyl-alcoholic solution:

$$l = 2,\ c = 1{\cdot}544,\ \alpha_D^{9{\cdot}5°} - 1{\cdot}78°,\ [\alpha]_D^{9{\cdot}5°} - 57{\cdot}6°.$$

Minguin does not quote the temperature at which his polarimetric observations were taken. The method he adopts for eliminating the excess of borneol from the ester does not appeal to us as being a satisfactory one, and he does not quote an analysis of his product.

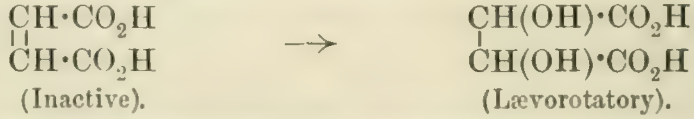
Since in the asymmetric synthesis accomplished by the aid of *l*-bornyl fumarate, the preponderance of potassium *l*-tartrate over potassium *d*-tartrate was so very slight, other experiments were tried in the hope of obtaining more convincing results. The oxidation of *l*-bornyl hydrogen fumarate proceeded in a much more satisfactory manner. This ester is obtained in small amount as a by-product from the preparation of the normal ester; a more convenient method for obtaining it in quantity is to submit the normal ester to half saponification with ethyl-alcoholic alkali. In the latter case, however, care must be taken to add water to the alcoholic alkali used, otherwise the bornyl group is displaced by the ethyl group to give ethyl hydrogen fumarate in place of the bornyl hydrogen fumarate desired. The asymmetric synthesis of *l*-tartaric acid was effected by oxidising potassium *l*-bornyl fumarate in aqueous solution by permanganate:



$$\begin{array}{c}CH{\cdot}CO_2H\\ \|\\ CH{\cdot}CO_2H\\ \text{(Inactive).}\end{array} \longrightarrow \begin{array}{c}CH{\cdot}CO_2{\cdot}C_{10}H_{17}\\ \|\\ CH{\cdot}CO_2H\\ \text{(Lævorotatory).}\end{array} \longrightarrow \begin{array}{c}CH{\cdot}CO_2{\cdot}C_{10}H_{17}\\ \|\\ CH{\cdot}CO_2K\\ \text{(Lævorotatory).}\end{array}$$

$$\longrightarrow \begin{array}{c}\overset{*}{C}H(OH){\cdot}CO_2{\cdot}C_{10}H_{17}\\ |\\ \overset{*}{C}H(OH){\cdot}CO_2K\\ \text{(Lævorotatory).}\end{array} \longrightarrow \begin{array}{c}\overset{*}{C}H(OH){\cdot}CO_2K\\ |\\ \overset{*}{C}H(OH){\cdot}CO_2K\\ \text{(Lævorotatory).}\end{array} \longrightarrow \begin{array}{c}\overset{*}{C}H(OH){\cdot}CO_2H\\ |\\ \overset{*}{C}H(OH){\cdot}CO_2H\\ \text{(Lævorotatory).}\end{array}.$$

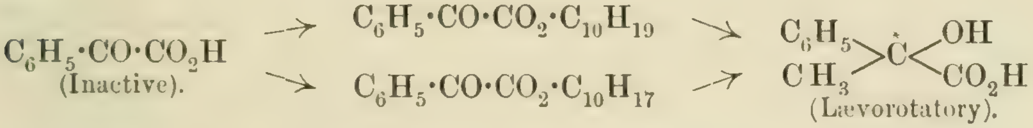
Here again a mixture of unequal amounts of *d*- and *l*- tartaric acids was obtained. It will be noted that the change



$$\begin{array}{c}CH{\cdot}CO_2H\\ \|\\ CH{\cdot}CO_2H\\ \text{(Inactive).}\end{array} \longrightarrow \begin{array}{c}CH(OH){\cdot}CO_2H\\ |\\ CH(OH){\cdot}CO_2H\\ \text{(Lævorotatory).}\end{array}$$

is possible by the introduction and subsequent complete elimination of the *l*-bornyl group.

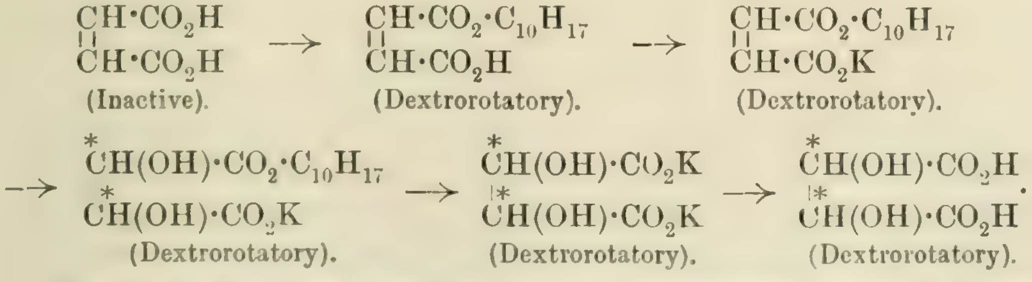
We also conducted an asymmetric synthesis of *l*-tartaric acid by means of *l*-menthol, using *l*-menthyl fumarate for the purpose. In previous papers, the difference between the *l*-menthyl and *l*-bornyl groups with regard to the extent of the asymmetric syntheses, which they bring about, has been indicated. *l*-Menthol is more lævorotatory than *l*-borneol, the values −49·4° and −39·7° respectively being obtained for their specific rotations in ethyl-alcoholic solutions, but the relative effect of the two groups in bringing about an asymmetric synthesis is quite out of proportion to the comparatively small difference in their optical activity. An example will make this clear. The asymmetric synthesis of atrolactinic acid has been accomplished by aid of Grignard's reagent either from *l*-menthyl benzoylformate or from *l*-bornyl benzoylformate (Trans., 1904, **85**, 1249; 1906, **89**, 365), thus:



$$\underset{\text{(Inactive).}}{C_6H_5\cdot CO\cdot CO_2H}\quad \begin{array}{c}\nearrow\ C_6H_5\cdot CO\cdot CO_2\cdot C_{10}H_{19}\ \searrow\\ \searrow\ C_6H_5\cdot CO\cdot CO_2\cdot C_{10}H_{17}\ \nearrow\end{array}\quad \underset{\text{(Lævorotatory).}}{\begin{array}{l}C_6H_5\\ CH_3\end{array}>\overset{*}{C}<\begin{array}{l}OH\\ CO_2H\end{array}}$$

Using 5 grams of *l*-menthyl benzoylformate, a lævorotatory mixture of *d*- and *l*-atrolactinic acids with $[\alpha]_D$ −8·5° in ethyl-alcoholic solution was obtained, whereas the acid mixture resulting from *l*-bornyl benzoylformate gave the value $[\alpha]_D$ −1·9° under similar conditions. Now, since the asymmetric synthesis of *l*-tartaric acid from the normal *l*-bornyl fumarate is so slight, it was anticipated that a better result would be obtained if the *l*-menthyl were substituted for the *l*-bornyl group. This we find to be the case. The oxidation of *l*-menthyl fumarate yields a mixture of potassium *d*- and *l*-tartrates, which is much more lævorotatory than when the bornyl group was used in the normal ester. The prediction is justifiable that *l*-menthyl hydrogen fumarate would exhibit a similar behaviour as contrasted with *l*-bornyl hydrogen fumarate, but we considered the results with the latter compound so conclusive that this experiment was not made.

It was, however, of interest to us to carry out the asymmetric synthesis of *d*-tartaric acid. This was accomplished by the aid of *d*-borneol according to the scheme:



$$\underset{\text{(Inactive).}}{\begin{array}{l}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{array}} \longrightarrow \underset{\text{(Dextrorotatory).}}{\begin{array}{l}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\end{array}} \longrightarrow \underset{\text{(Dextrorotatory).}}{\begin{array}{l}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2K\end{array}}$$

$$\longrightarrow \underset{\text{(Dextrorotatory).}}{\begin{array}{l}\overset{*}{C}H(OH)\cdot CO_2\cdot C_{10}H_{17}\\ \overset{*}{C}H(OH)\cdot CO_2K\end{array}} \longrightarrow \underset{\text{(Dextrorotatory).}}{\begin{array}{l}\overset{*}{C}H(OH)\cdot CO_2K\\ |\\ \overset{*}{C}H(OH)\cdot CO_2K\end{array}} \longrightarrow \underset{\text{(Dextrorotatory).}}{\begin{array}{l}\overset{*}{C}H(OH)\cdot CO_2H\\ |\\ \overset{*}{C}H(OH)\cdot CO_2H\end{array}}.$$

Finally, it may be stated that certain precautions, some of them rather obvious, were observed throughout in order to ensure that the rotations, on which our conclusions are based, were not due to other causes than asymmetric synthesis:

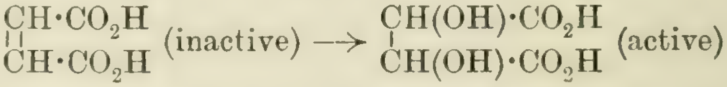
(1) The fumaric acid used was optically inactive, as it ought to be.

(2) The rotations, observed after removal of the borneol (or menthol) subsequently to the saponification, were not due to traces of borneol or menthol. The complete removal of borneol or menthol from the product of saponification of bornyl or menthyl esters is not difficult to effect (compare Trans., 1904, **85**, 378, 1249; 1905, **87**, 1004, 1373; 1906, **89**, 365, 688).

(3) The rotations observed were not due to resolution by the biological method. Care was always taken to prevent any appreciable micro-organism growth in the solutions under investigation.

(4) The esters, *l*-bornyl fumarate, &c., used as the starting point of the syntheses, yield optically inactive solutions on saponification and removal of the active alcohol.

(5) The rotations observed were not due to fractional saponification (Marckwald and McKenzie). It is conceivable, for example, that when *l*-bornyl hydrogen fumarate is oxidised, it might be converted into *l*-bornyl hydrogen *r*-tartrate, a partially racemic ester, which in solution consists of equal amounts of *l*-bornyl hydrogen *d*-tartrate, and *l*-bornyl hydrogen *l*-tartrate. If an ester of this type is saponified by an excess of alkali, racemic acid would result; if an insufficiency of alkali is used, a mixture of unequal amounts of *d*- and *l*-tartaric acids might result. The change



$$\begin{array}{l}\mathrm{CH{\cdot}CO_2H}\\ \|\\ \mathrm{CH{\cdot}CO_2H}\end{array}\text{ (inactive) }\longrightarrow\begin{array}{l}\mathrm{CH(OH){\cdot}CO_2H}\\ |\\ \mathrm{CH(OH){\cdot}CO_2H}\end{array}\text{ (active)}$$

could therefore be brought about by this method, which, however, it must be distinctly borne in mind, is not an asymmetric synthesis.

It was accordingly necessary for us to make certain that the saponification of the product of oxidation was in each case complete and that no fractional saponification took place.

(6) The rotations observed were not due to resolution by crystallisation.

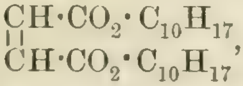
EXPERIMENTAL.

Oxidation of l-*Bornyl Fumarate.*

The fumaric acid used for the preparation of *l*-bornyl fumarate was obtained from Kahlbaum. It was analysed and the necessary precaution taken to ensure that it was optically inactive.

The *l*-borneol used was obtained from Schimmel & Co., and was prepared by them from *Blumea balsamifera.* Its specific rotation in ethyl-alcoholic solution was in accordance with the results quoted in the literature.

A finely-powdered mixture of fumaric acid (1 mol.) and *l*-borneol (2½ mol.) was heated in a paraffin bath at 150—160° for twenty-four hours. The extent of the esterification depends largely on the manner in which the heating is conducted; in one experiment, for example, where 50 grams of fumaric acid were used, 28 grams were unesterified; in a second experiment, using the same weight of acid, 19 grams were unesterified, whilst, in a third experiment, the esterification was practically complete. In order to obtain a good yield of the normal ester, the mixture should be repeatedly shaken and the sublimed borneol prevented from accumulating in the neck of the flask. The bulk of the unesterified fumaric acid was then removed by shaking the semi-solid mass with ether, in which fumaric acid is sparingly soluble. After shaking the ethereal solution, first with a dilute aqueous solution of sodium carbonate and then with water in order to remove the acid-ester and the free acid present, the ether was expelled from the neutral solution and the residue submitted to distillation in a current of steam for several hours in order to remove the excess of borneol. Although the ester undergoes practically no saponification under this treatment, the contents of the flask were extracted with ether, the ethereal solution washed with sodium carbonate and then dried with calcium chloride. The solid, remaining after evaporation of the ether, was crystallised from ethyl alcohol. In one experiment, the yield of ester from 50 grams of fumaric acid was 102 grams.

l-*Bornyl fumarate*,  $\begin{array}{l}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2\cdot C_{10}H_{17}\end{array}$, is moderately soluble in cold ethyl alcohol (100 c.c. of solution at 10° contain about 1·6 grams), easily soluble in hot ethyl alcohol; it separates in colourless, transparent, stellate needles, m. p. 106°.

0·1456 gave 0·3967 CO_2 and 0·1225 H_2O. $C = 74{\cdot}3$; $H = 9{\cdot}4$.

$C_{24}H_{36}O_4$ requires $C = 74{\cdot}2$; $H = 9{\cdot}3$ per cent.

A determination of its molecular weight by the cryoscopic method in benzene solution gave the value 378 (calculated 388).

Its specific rotation was determined in chloroform and in ethyl-alcoholic solutions respectively:

In chloroform, $l = 2$, $c = 5{\cdot}2764$, $\alpha_D^{10\cdot5^\circ}$ $-6{\cdot}55^\circ$, $[\alpha]_D^{10\cdot5^\circ}$ $-62{\cdot}1^\circ$.

In ethyl alcohol, $l = 2$, $c = 1{\cdot}544$, $\alpha_D^{9\cdot5^\circ}$ $-1{\cdot}78^\circ$, $[\alpha]_D^{9\cdot5^\circ}$ $-57{\cdot}6^\circ$.

The ester is very readily soluble in cold carbon disulphide, carbon tetrachloride or benzene, easily so in cold ether, chloroform, or pyridine, moderately so in cold glacial acetic acid, light petroleum or acetone, sparingly so in cold methyl alcohol and insoluble in water.

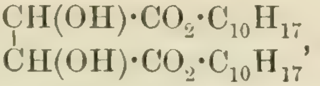
l-Bornyl fumarate (25 grams) was dissolved in 2 litres of glacial acetic acid and an aqueous solution of potassium permanganate (350 c.c., containing 7 grams) run in during half an hour with brisk stirring. The colourless solution, together with a flocculent white precipitate, which had separated, was evaporated nearly to dryness on the water-bath, water added to the residue and the whole extracted with ether for seven hours in a Hagemann apparatus. After this treatment, the white precipitate, which remained undissolved in contact with the aqueous layer, was separated and boiled for six hours with ether, whilst the aqueous solution was submitted to a further extraction in the Hagemann apparatus for six hours. There were thus obtained: (*a*) a white precipitate, (*b*) an aqueous solution, and (*c*) an ethereal solution. The white precipitate (*a*) contained manganese, and its solution in hydrochloric acid was optically inactive. The aqueous solution (*b*), when evaporated to small bulk, also proved on polarimetric examination to be optically inactive. The ethereal solution (*c*) was then treated as follows. The ester mixture, obtained after the removal of the ether, was saponified by the addition of a solution of 18·3 grams of potassium hydroxide in 250 c.c. of ethyl alcohol. After remaining for two hours at the ordinary temperature, the product was boiled for one hour under a reflux condenser, a little water having been added to dissolve the potassium salt which separated. The ethyl alcohol was then removed, water added, the precipitated borneol drained off and the filtrate extracted several times with ether to remove traces of borneol. The alkaline aqueous solution was neutralised by hydrochloric acid and then concentrated on the water-bath. From the experience of one of us with the saponification of bornyl esters and the removal of free borneol from the products of saponification, it was concluded that no borneol could be present after the treatment described. The resulting solution (28 c.c.) was polarimetrically examined, 7 c.c. of it in a 1-dcm. tube giving α_D $-0·09°$. The half-shadow arrangement of our polarimeter was so adjusted that the readings of the solution could be taken with certainty to within $\pm 0·01°$; when the instrument was set at zero and the tube containing the above solution introduced, the dark shadow in the centre of the triple field at once appeared. The solution was then acidified with hydrochloric acid. The precipitate which settled was inactive and contained fumaric acid; the filtrate (27 c.c.) was lævorotatory, 16 c.c. of it in a 2-dcm. tube giving $-0·07°$. The acid solution was freed from hydrochloric acid by evaporation, neutralised by ammonia, lead acetate added, the precipitated lead salt separated and suspended in water and then decomposed by hydrogen sulphide. The aqueous filtrate was again distinctly lævorotatory.

The experiment was repeated. Ten grams of ester were dissolved in 500 c.c. of glacial acetic acid and the oxidation was conducted by adding 100 c.c. of permanganate, containing 2 grams of salt. In this case the acetic acid was removed under diminished pressure. Evidence of the asymmetric synthesis of *l*-tartaric acid was again obtained, the observed rotations being of the same order as those quoted in the first experiment.

As confirmatory evidence that the slight activity observed was actually due to an asymmetric synthesis, it was considered desirable to saponify the normal ester without first oxidising it, in order to show that the resulting potassium salt is inactive. This was done with 10 grams of *l*-bornyl fumarate, which was dissolved in 50 c.c. of ethyl alcohol and boiled for one hour with a solution of 5·3 grams of potassium hydroxide in 100 c.c. of ethyl alcohol. The ethyl alcohol and borneol were removed as usual, and the aqueous solution of potassium salt shown to be absolutely inactive.

In another experiment the ester was oxidised with the object of finding out whether any of it had survived the attack of the permanganate. The conditions of the oxidation were similar to those employed in the first of the experiments already referred to. The examination of the product showed that it contained, in addition to a very little *l*-bornyl *l*-tartrate, both unchanged fumarate and *l*-bornyl *r*-tartrate, a conclusion arrived at after we had prepared the latter compound as follows.

An intimate mixture of dehydrated racemic acid (20 grams) and *l*-borneol (70 grams) was heated in a paraffin bath at 120—130° for about forty hours, a current of dry hydrogen chloride having been passed into the mixture at intervals. The resulting jelly was dissolved in ether, the ethereal solution washed with aqueous sodium carbonate and finally with water, the ether removed, and the bulk of the borneol separated by steam distillation. The yield of the crude ester was about 50 grams. It is easily purified by crystallisation from methyl alcohol.

l-*Bornyl* r-*tartrate*,  $\begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ | \\ CH(OH)\cdot CO_2\cdot C_{10}H_{17}\end{matrix}$, is readily soluble in hot and sparingly so in cold methyl alcohol, from which it separates on slow crystallisation in well-defined blunt needles, melting at 115·5—116°:

0·1488 gave 0·3701 CO_2 and 0·1206 H_2O. C = 67·8 ; H = 9·0.

$C_{24}H_{38}O_6$ requires C = 68·2 ; H = 9·1 per cent.

Its specific rotation was determined in chloroform solution:

$$l = 2,\ c = 3{\cdot}9608,\ a_D^{10\cdot5}\ -3{\cdot}05^\circ,\ [a]_D^{10\cdot5}\ -38{\cdot}5^\circ.$$

The ester is readily soluble in cold chloroform, carbon tetrachloride, carbon disulphide, ethyl alcohol, ether, or benzene, sparingly so in cold light petroleum, and very insoluble in water. It is partially racemic.

When crystallised eight times from methyl alcohol, its melting point had not altered and its specific rotation in chloroform solution was practically the same:

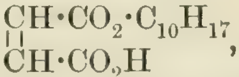
$$l=2,\ c=6{\cdot}2232,\ \alpha_D^{11\cdot5^\circ}\ -4{\cdot}84^\circ,\ [\alpha]_D^{11\cdot5^\circ}\ -38{\cdot}9^\circ.$$

In solution it is doubtless resolved into a mixture of equal amounts of *l*-bornyl *d*-tartrate and *l*-bornyl *l*-tartrate, two diastereoisomeric esters which may be expected to possess different solubilities. It was, therefore, possible on theoretical grounds that fractional crystallisation of the racemate would give either the *d*-tartrate or the *l*-tartrate as the more sparingly soluble product, but this was not the case in the experiment we tried. Similar attempts to resolve a partially racemic ester have been made by Frankland and Price (Trans., 1897, **71**, 253) with *d*-amyl *r*-dibenzoylglycerate, and by one of us (Trans., 1904, **85**, 384) with *l*-menthyl *r*-mandelate.

Oxidation of l-*Bornyl Hydrogen Fumarate.*

For the preparation of the acid-ester, the aqueous sodium carbonate containing it (see preparation of the normal ester) was acidified by an excess of hydrochloric acid, extracted with ether and the ethereal solution dried over sodium sulphate. The residue, after evaporation of the ether, was extracted by boiling light petroleum (b. p. 60—80°), by which treatment the fumaric acid present remained undissolved. The acid-ester separated from the light petroleum solution and was purified by recrystallisation from the same solvent. Since fumaric acid is practically insoluble in chloroform, the latter solvent may also conveniently be used in order to effect the separation; the chloroform is then expelled and the residue crystallised with light petroleum.

The ester may also be prepared by the half saponification of the normal ester according to the method indicated later for obtaining *d*-bornyl hydrogen fumarate.

l-*Bornyl hydrogen fumarate,* 
$\begin{matrix}\mathrm{CH{\cdot}CO_2{\cdot}C_{10}H_{17}}\\ \|\\ \mathrm{CH{\cdot}CO_2H}\end{matrix}$, separates from light petroleum in glistening leaflets, m. p. 116·5—117°.

0·1500 gave 0·3658 CO_2 and 0·1102 H_2O. C = 66·5; H = 8·2.

$C_{14}H_{20}O_4$ requires C = 66·6; H = 8·0 per cent.

Its specific rotation was determined in chloroform and in ethyl-alcoholic solutions respectively:

In chloroform, $l=2,\ c=6{\cdot}786,\ \alpha_D^{12^\circ}\ -6{\cdot}61^\circ,\ [\alpha]_D^{12^\circ}\ -48{\cdot}7^\circ.$

In ethyl alcohol, $l=2,\ c=4{\cdot}0506,\ \alpha_D^{11\cdot5^\circ}\ -3{\cdot}63^\circ,\ [\alpha]_D^{11\cdot5^\circ}\ -44{\cdot}8^\circ.$

The ester is very readily soluble in cold chloroform, carbon tetrachloride, ether, methyl alcohol, ethyl alcohol, acetone, carbon disulphide, pyridine, or glacial acetic acid, less readily so in cold benzene, and sparingly so in water.

l-Bornyl hydrogen fumarate (8·7 grams) was dissolved in a solution of 3 grams of potassium carbonate in 100 c.c. of water and the whole made up to about 1 litre with water. A solution of 5 grams of potassium permanganate in 250 c.c. of water was added drop by drop within an interval of three hours, the oxidation being conducted at 2—3° with brisk stirring. After the precipitated manganese dioxide had been drained off, the solution was nearly neutralised by hydrochloric acid and then concentrated by evaporation. It was then acidified by an excess of hydrochloric acid and extracted with ether in a Hagemann apparatus for about nine hours. The aqueous layer was concentrated to small bulk and proved to be quite inactive towards polarised light. The ether was removed from the ethereal solution and the residue treated with a solution of 5·2 grams of potassium hydroxide in 100 c.c. of ethyl alcohol. After two hours at the ordinary temperature, 10 c.c. of water were added and the whole boiled for one hour under a reflux apparatus. At the end of this time the solution was strongly alkaline. The ethyl alcohol was removed, water added, the precipitated borneol drained off, the aqueous filtrate extracted several times with ether, and then nearly neutralised by hydrochloric acid. After concentration by evaporation the aqueous solution of potassium salts (18 c.c.) thus obtained was lævorotatory, 16 c.c. of it in a 2-dcm. tube giving a_D − 0·56°. On acidifying this with hydrochloric acid the white precipitate, which settled, consisted of fumaric acid, racemic acid, and *l*-tartaric acid; its solution (16 c.c.) in aqueous sodium hydroxide gave a_D − 0·34° in a 2-dcm. tube. (The presence of fumarate together with the tartrates in this product was shown by the behaviour of the solution towards permanganate and by an analysis of the silver salt, which gave Ag = 62·3, whereas silver tartrate requires 59·3 and silver fumarate 65·4 per cent.) The filtrate, from which the solid had been separated, gave a_D − 0·14° in a 2-dcm. tube when evaporated to 16 c.c.; it was made alkaline by aqueous potassium hydroxide, and the solution of potassium salt (16 c.c.) gave a_D − 0·21°.

The whole of the aqueous solution containing the product of the asymmetric synthesis was neutralised and converted into lead salt (compare oxidation of *l*-bornyl fumarate). The acid, obtained from this lead salt, was also lævorotatory, and gave the ordinary qualitative tests which one would expect from a mixture of racemic and *l*-tartaric acids (reducing action, insolubility of calcium salt, &c.).

In a second experiment, 17 grams of acid-ester were oxidised in a similar manner by a solution of 7 grams of potassium permanganate in 350 c.c. of water. In this case the solution of potassium salt, obtained after the complete removal of borneol, was concentrated to a volume of 20 c.c., of which 16 c.c. in a 2-dcm. tube gave a_D − 0·71°. When this solution was acidified by hydrochloric acid a white precipitate separated; the filtrate was lævorotatory, and became more so when made alkaline (compare preceding experiment).

The acid-ester was also saponified by alcoholic potassium hydroxide without having first been oxidised (compare experiment previously quoted with the normal ester). The borneol was eliminated as usual, and the aqueous solution of potassium salt shown to be quite inactive.

It was noted that, in all the cases of the asymmetric synthesis of the optically active tartaric acids quoted in the present paper, the optical activity of the aqueous solution of potassium salt (containing the excess of active tartrate) is greater than the activity of the solution, obtained on its acidification by a mineral acid, provided, of course, that due account is taken of the relative concentrations of the solutions in question. This is in accordance with the fact that the specific rotation of *d*-tartaric acid in water, $[\alpha]_D^{20^\circ}$ 15·06° − 0·131 *c* ($c = 0·5$ to 15), as determined by Landolt (*Ber.*, 1873, **6**, 1073), is less than that of its potassium salt, which has $[\alpha]_D^{20^\circ}$ 29·19° for $c = 20·38$ (Thomsen, *J. pr. Chem.*, 1886, [ii], **34**, 89).

Oxidation of l-*Menthyl Fumarate.*

For the preparation of this ester, fumaric acid was heated with three times its weight of *l*-menthol in a paraffin-bath at 150—160° for thirty-two hours, at the end of which time a little solid fumaric acid still remained. The viscid, brown jelly obtained was dissolved in ether, washed with sodium carbonate and water to free it from the acid-ester, and the menthol removed either by steam distillation or by distillation under diminished pressure. The crude ester was obtained as a very viscid, brown product, practically insoluble in water; we did not succeed in obtaining it in any other form than an oil. It was not analysed. The oxidation was conducted as follows. Twenty-four grams were dissolved in 900 c.c. of glacial acetic acid and a solution of 6·6 grams of potassium permanganate in 300 c.c. of water gradually added, with constant stirring, within an interval of five hours. After the product was evaporated on the water-bath, it was extracted with ether, the ether expelled, and the ester mixture saponified by being heated for two hours with a solution of 11 grams of potassium hydroxide in 200 c.c. of ethyl alcohol. The alkali was in excess. The ethyl alcohol was expelled, water added, the precipitated menthol removed by filtration, the filtrate extracted several times with ether, and then heated on the water-bath for some time. By this treatment the menthol was completely removed. The aqueous solution of potassium salt obtained in this manner was too coloured to permit of exact polarimetric examination, and it was not possible to decolorise it in alkaline solution. In presence of excess of hydrochloric acid, however, it was decolorised by animal charcoal; the solution (70 c.c.) was then found to be lævorotatory, 16 c.c. of it in a 2-dcm. tube giving a_D $-0\cdot19^\circ$. The lead salt obtained from it was decomposed by hydrogen sulphide, and an aqueous solution giving a_D $-0\cdot22^\circ$ in a 2-dcm. tube was obtained from it.

Several other experiments were conducted, and the results were similar to that just quoted.

Oxidation of d-*Bornyl Hydrogen Fumarate.*

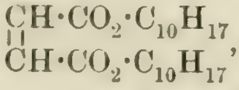
Experiments with the fumarates of *l*-borneol having shown that the acid-ester is more suitable than the normal ester for purposes of asymmetric synthesis, the acid-ester of *d*-borneol was used for the asymmetric synthesis of *d*-tartaric acid.

Whilst *l*-borneol is easily obtained from naturally occurring sources, Schimmel and Co. were unable to provide us with *d*-borneol, the source of which is quoted in the literature as being *Dryobalanops camphora*. The product, obtained by the reduction of camphor, is not homogeneous, although it has the superficial appearance of being pure and is very often used as if it were. The borneol we obtained from Kahlbaum had $[a]_D^{18^\circ}$ $+23^\circ$ ($c=18\cdot144$) in ethyl-alcoholic solution, whereas pure *d*-borneol has $[a]_D$ $+37^\circ$ for about the same concentration in the same solvent. This product from camphor is a solid solution of *d*-borneol and *iso*borneol, and is practically unchanged after repeated crystallisation from light petroleum. It appears from the recent work of Hesse (*Ber.*, 1906, 39, 1127) that *iso*borneol is not a tertiary alcohol as was formerly supposed, but a secondary alcohol, stereoisomeric with *d*-borneol.

We are indebted to Dr. R. H. Pickard for the suggestion that when Kahlbaum's product is heated in benzene solution with zinc chloride, a mixture is obtained from which *d*-borneol is easily separated by crystallisation from light petroleum. By this method we obtained *d*-borneol, having the following rotation in ethyl-alcoholic solution:

$$l=2,\ c=16\cdot975,\ a_D\ +12\cdot22^\circ,\ [a]_D\ +36\cdot6^\circ.$$

The normal *d*-fumarate was prepared by the method already described for the *l*-fumarate. Fumaric acid (72 grams) was heated with *d*-borneol (145 grams) for several days at 150—160°. The unesterified fumaric acid weighed 28 grams; the yield of pure ester, after crystallisation from ethyl alcohol, was 100 grams. The yield of acid ester, which was separated from fumaric acid by means of chloroform, was 7·5 grams.

d-*Bornyl fumarate*,  $\begin{array}{l}CH\cdot CO_2\cdot C_{10}H_{17}\\ \parallel\\ CH\cdot CO_2\cdot C_{10}H_{17}\end{array}$, melted at 106—107° and closely resembled the enantiomorphous *l*-ester:

0·1832 gave 0·4984 CO_2 and 0·1534 H_2O. C = 74·2; H = 9·4.

$C_{24}H_{36}O_4$ requires C = 74·2; H = 9·3 per cent.

Determination of its specific rotation in chloroform and ethyl-alcoholic solutions respectively gave values in satisfactory agreement with those previously obtained with the *l*-ester:

In chloroform, $l = 1$, $c = 5·398$, $a_D^{10°}$ + 3·31°, $[a]_D^{10°}$ + 61·3°.

In ethyl alcohol, $l = 1$, $c = 1·622$, $a_D^{10°}$ + 0·93°, $[a]_D^{10°}$ + 57·3.

In order to obtain a larger amount of the acid ester, the normal ester was submitted to half-saponification by alkali in alcoholic solution. At first the results were not satisfactory, since ethyl hydrogen fumarate was obtained together with only a little of the *d*-bornyl hydrogen fumarate, replacement of the *d*-bornyl group by the ethyl group having taken place under the influence of the alcoholic potassium hydroxide. This result recalls the experience of Purdie (Trans., 1888, **53**, 391, &c.) on the displacement of alkyl groups in esters under the influence of a trace of alkyloxide, and one experiment is worth quoting:

Twenty grams of *d*-bornyl fumarate were dissolved by heating with 70 c.c. of ethyl alcohol and 40 c.c. of ethyl-alcoholic sodium hydroxide (1 c.c. = 0·0512 NaOH) added to the hot solution. After being heated for two hours, the solution was neutral. The alcohol was expelled at the temperature of a boiling-water bath, water added, and the mixture of unchanged normal ester and the *d*-borneol separated from the aqueous solution by extracting with ether several times. The aqueous solution was acidified with dilute sulphuric acid, extracted with ether, and the product, after expulsion of the ether, extracted with chloroform. The chloroform solution was dried by sodium sulphate, the chloroform expelled, and the residue crystallised from light petroleum (b. p. 60—80°). The crop, which separated slowly, consisted of tiny needles different in appearance from that of the characteristic lustrous bornyl acid-ester. When crystallised twice from light petroleum, the product was found to be ethyl hydrogen fumarate. It melted at 69—70°, whereas Shields (Trans., 1891, **59**, 738) gives 70°:

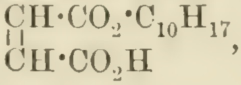
0·1943 gave 0·3546 CO_2 and 0·0972 H_2O. C = 49·8; H = 5·6.

$C_6H_8O_4$ requires C = 50·0; H = 5·6 per cent.

From the filtrates, from which ethyl hydrogen fumarate had been removed, a small amount of *d*-bornyl hydrogen fumarate was isolated.

This displacement of the *d*-bornyl by the ethyl group is, however, easily prevented if a little water is added to the alcoholic alkali used in the half-saponification. The following method may conveniently be used for the preparation of *d*-bornyl hydrogen fumarate.

To a hot solution of 20 grams of *d*-bornyl normal fumarate in 70 c.c. of ethyl alcohol, a mixture of 30 c.c. of water and 40 c.c. of ethyl-alcoholic sodium hydroxide (1 c.c. = 0·0512 NaOH) is added and the mixture kept boiling gently for one hour. The alcohol is then removed as quickly as possible, water added, and the mixture extracted with ether several times. The ether is then expelled from the neutral aqueous solution, an excess of dilute sulphuric acid added, and the turbid solution extracted twice with chloroform. The chloroform solution is dried, the chloroform expelled, and the residue crystallised from light petroleum (b. p. 60—80°). The acid-ester separated quickly in characteristic lustrous plates, which closely resemble in general properties the *l*-bornyl hydrogen fumarate already described. The yield, 5·6 grams, is satisfactory. The ester may also be recrystallised from benzene, from which it separates in glassy plates.

d-*Bornyl hydrogen fumarate,*  $\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\end{matrix}$, melting at 117—118°, was analysed:

0·1694 gave 0·4152 CO_2 and 0·1212 H_2O. C = 66·8; H = 8·0.
$C_{14}H_{20}O_4$ requires C = 66·6; H = 8·0 per cent.

A determination of its specific rotation in chloroform solution gave the value:

$l = 2$; $c = 5{\cdot}678$; α_D^{15} $+5{\cdot}37°$; $[\alpha]_D^{15}$ $+47{\cdot}3°$.

The asymmetric synthesis of *d*-tartaric acid was accomplished as follows.

d-Bornyl hydrogen fumarate (14·3 grams) was dissolved in 100 c.c. of water containing 4·3 grams of potassium carbonate and 500 c.c. of water added. A solution of 8·2 grams of potassium permanganate in 600 c.c. of water was added with brisk stirring during one and a half hours at the ordinary temperature. After two days, the precipitated manganese dioxide was filtered off and washed with water. The colourless filtrate was then neutralised by hydrochloric acid and evaporated to dryness. The residual solid was added to a solution of 5 grams of potassium hydroxide in 100 c.c. of the methyl alcohol, the mixture boiled for half an hour, 40 c.c. water added, and the heating continued for an hour longer. The methyl alcohol was expelled, water added, and the product extracted several times with ether, the ethereal solution containing, of course, practically all the borneol. The aqueous solution was completely freed from borneol by the usual method, having previously been neutralised by the addition of hydrochloric acid. The solution (75 c.c.) was dextrorotatory, 16 c.c. of it in a 2-dcm. tube giving α_D $+0{\cdot}28°$. On further evaporation, a little potassium chloride separated; this was filtered off and the filtrate (25 c.c.) was examined in the 2-dcm. tube, containing 16 c.c., when the value α_D $+0{\cdot}72°$ was obtained. The acid obtained from this solution by the agency of the lead salt was also distinctly dextrorotatory in aqueous solution.

Ten grams of *d*-bornyl hydrogen fumarate, when saponified by an excess of alcoholic potassium hydroxide, gave an optically inactive potassium salt after the borneol had been removed.

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CXIII.—*Calmatambin: a New Glucoside.*

By FRANK LEE PYMAN.

THE natives of Sierra Leone use as a medicine the bark of a tree which they call *Calmatamba*, and which is probably identical with *Canthium glabrifolium.* In the course of a chemical examination of the bark, a new crystalline glucoside, *calmatambin*, has been isolated in a quantity amounting to 1·1 per cent. of its weight. This has the formula $C_{19}H_{28}O_{13},2H_2O$, and crystallises in colourless, prismatic needles melting at 100°. The anhydrous substance melts at 144—145°. It is lævorotatory, $[\alpha]_D - 130{\cdot}4°$, and contains one methoxyl group.

On acetylation it yields *octa-acetylcalmatambin*,

$$C_{19}H_{20}O_{13}(C_2H_3O)_8,$$

which crystallises in needles melting at 179—180° and has $[\alpha]_D - 107{\cdot}1°$.

When calmatambin is hydrolysed with acids, dark brown decomposition products are formed, and it has been possible to identify only dextrose, but on subjecting it to the action of emulsin for several days at 40°, hydrolysis occurs with the formation of dextrose and a new substance, *Calmatambetin*, $C_{13}H_{18}O_8$, in accordance with the equation:

$$C_{19}H_{28}O_{13} + H_2O = C_6H_{12}O_6 + C_{13}H_{18}O_8.$$

Calmatambin is therefore a β-glucoside.

Calmatambetin crystallises in needles containing one-half a molecular proportion of water and melts at 148—149°. It contains one methoxyl group and is optically inactive. It is readily resinified on treatment with acids or alkalis, but, when distilled with 1 per cent. hydrochloric acid, yields a small quantity of a scarlet, crystalline *substance*, $C_{11}H_{12}O_3$, melting at 91°, which it has not been possible to identify. This substance has an aromatic odour and is volatile with steam, and these facts, considered in conjunction with the fact of its deep colour, suggest that the substance might be a quinone; the quantity available was, however, insufficient for further investigation.

From the foregoing facts it follows that calmatambin is the β-dextrose ether of calmatambetin, and must have the constitution represented by the following formula:

$$CH_3{\cdot}O{\cdot}C_{12}H_{10}O_2(OH)_4{\cdot}O{\cdot}C_6H_{11}O_5.$$

Calmatambetin may then be expressed as follows:

$$CH_3{\cdot}O{\cdot}C_{12}H_{10}O_2(OH)_5.$$

Calmatambin is physiologically inactive.

EXPERIMENTAL.

Isolation of Calmatambin, $C_{19}H_{28}O_{13},2H_2O$.

The powdered bark was extracted with ten times its weight of ethyl acetate. On the removal of the solvent a syrup remained which was dissolved in a little hot water and poured into a large excess of cold water. This caused the precipitation of the bulk of the resin, and the remainder was removed by treatment with lead subacetate solution. The solution was then freed from lead by means of hydrogen sulphide, and evaporated on the water-bath to a thin, dark brown syrup which was dried in a vacuum desiccator over sulphuric acid and completely extracted by dry ethyl acetate. The ethyl acetate solutions were moistened while still hot by the addition of 1 c.c. water for each 300 c.c. solution, and the glucoside separated on cooling in glistening, colourless prismatic needles in a quantity amounting to 1·1 per cent. of the weight of the bark. The glucoside thus obtained is pure, and when dried in the air melts at 100°; when dried in a vacuum over sulphuric acid or at 95° it loses two molecules of water of crystallisation and melts at 144—145°. For analysis it was recrystallised from moist ethyl acetate and dried in the air.

0·1831 gave 0·3062 CO_2 and 0·1112 H_2O. C = 45·6; H = 6·8.
0·1670 ,, 0·2771 CO_2 ,, 0·0983 H_2O. C = 45·3; H = 6·6.
0·1913 ,, 0·3185 CO_2 ,, 0·1134 H_2O. C = 45·4; H = 6·6.
0·2037 gave, by Zeisel's method, 0·1040 AgI. OMe = 6·8.
0·2861 ,, ,, ,, 0·1434 AgI. OMe = 6·6.
0·2439, dried in a vacuum over sulphuric acid, lost 0·0182. H_2O = 7·5.
0·3205, dried at 95°, lost 0·0243. H_2O = 7·6.
0·2407, ,, ,, 0·0179. H_2O = 7·4.

$C_{19}H_{28}O_{13},2H_2O$ requires C = 45·6; H = 6·5; OMe = 6·2; H_2O = 7·2 per cent.

The anhydrous substance was also analysed:

0·1933 gave 0·3472 CO_2 and 0·1122 H_2O. C = 49·0; H = 6·5.

0·1682 gave 0·3026 CO_2 and 0·0980 H_2O. C = 49·1 ; H = 6·5.
0·2228 „ 0·4039 CO_2 „ 0·1280 H_2O. C = 49·4 ; H = 6·4.
$C_{19}H_{28}O_{13}$ requires C = 49·1 ; H = 6·1 per cent.

The molecular weight of calmatambin was very kindly determined by Dr. Barger by his microscopical method (Trans., 1904, **85**, 286).

A solution containing 0·18 gram of air-dried calmatambin in 2·0 grams of water was intermediate between 0·18 and 0·19 mol. sucrose as standard at the ordinary temperature, whence M = 474—500, mean 487.

$C_{19}H_{28}O_{13},2H_2O$ requires M = 500.

A solution of 0·4295 gram air-dried calmatambin in water made up to 8·2 c.c. gave α_D – 6·83° in a 1-dcm. tube, whence $[\alpha]_D$ – 130·4°.

Calmatambin is readily soluble in water or alcohol, and sparingly so in warm ethyl acetate; it is insoluble in all the other usual organic solvents. It does not reduce Fehling's solution, is not precipitated by lead subacetate solution, and gives no coloration with ferric chloride or concentrated nitric acid. It dissolves in cold concentrated sulphuric acid, giving a pale green solution which becomes carmine on adding an equal volume of water.

Calmatambin is hydrolysed by boiling dilute acids, giving dextrose (identified as phenyl-*d*-glucosazone, m. p. 206°) and dark brown decomposition products from which no crystalline substance could be isolated; it is readily hydrolysed by emulsin, but not by yeast.

When fused with potassium hydroxide at 150° a dark brown mass resulted, from which no crystalline product could be obtained.

Octa-acetylcalmatambin, $C_{19}H_{20}O_{13}(C_2H_3O)_8$.

Calmatambin is readily acetylated by boiling for half an hour with an excess of acetic anhydride and a small amount of anhydrous sodium acetate. The acetyl derivative was purified by crystallisation from absolute alcohol, from which it separated in long white needles melting at 179—180°. It is readily soluble in hot alcohol or chloroform, but is insoluble in water.

0·1890 gave 0·3624 CO_2 and 0·0970 H_2O. C = 52·3 ; H = 5·8.
0·2527 „ 0·4820 CO_2 „ 0·1269 H_2O. C = 52·0 ; H = 5·6.
$C_{19}H_{20}O_{13}(C_2H_3O)_8$ requires C = 52·5 ; H = 5·6.

The number of acetyl groups was determined by A. G. Perkin's ethyl acetate method (Trans., 1905, **87**, 107).

0·2725 gave 0·1637 acetic acid. $C_2H_4O_2$ = 60·1.
$C_{19}H_{20}O_{13}(C_2H_3O)_8$ requires $C_2H_4O_2$ = 60·0 per cent.

A solution of 0·4201 gram in chloroform made up to 10 c.c. gave α_D – 4·50° in a 1-dcm. tube, whence $[\alpha]_D$ – 107·1°.

Hydrolysis of Calmatambin by Emulsin. Formation of Calmatambetin and Dextrose.

Six grams of calmatambin were dissolved in 60 c.c. of water and 0·6 gram of emulsin added. The solution was maintained at 40° for three days, and then completely extracted with ether. The ethereal extract consisted of 1·7 grams of white, prismatic needles melting at 148—149°. The mother liquor was freed from ether and again subjected to the action of emulsin at 40° for three days, and gave on extraction with ether a further quantity of 0·4 gram of hydrolytic product melting at 148—149°. The total yield of calmatambetin, 2·1 grams, represents 52 per cent. of the theoretical.

The dark brown mother liquor was then evaporated to dryness, extracted with hot ethyl acetate to remove the last traces of calmatambetin, and treated with hot absolute alcohol. On the removal of the alcohol a yellow syrup remained; this was dissolved in water, and the solution, on treatment with phenylhydrazine and acetic acid, gave an osazone melting at 206°. This was identified as phenyl-*d*-glucosazone, since a mixture of equal parts of this substance and pure phenyl-*d*-glucosazone melted simultaneously at 206°. The sugar is therefore dextrose.

Calmatambetin, $C_{13}H_{18}O_8,\frac{1}{2}H_2O$.

This substance is obtained pure by the above method, since after recrystallisation from ethyl acetate it melts at 148—149°. The air-dried substance contains water of crystallisation, but the amount is somewhat variable. The following figures represent the percentage of water lost by the air-dried substance at 100°:

3·7, 3·1, 2·8, 3·6, 2·1, 3·5.

$C_{13}H_{18}O_8,\frac{1}{2}H_2O$ requires $H_2O = 2·9$ per cent.

After being dried at 100°:

0·2304 gave 0·4382 CO_2 and 0·1274 H_2O. C = 51·9; H = 6·2.

0·2318 „ 0·4388 CO_2 „ 0·1252 H_2O. C = 51·6; H = 6·1.

0·2210 gave, by Zeisel's method, 0·1699 AgI. OMe = 10·2.

$C_{13}H_{18}O_8$ requires C = 51·6; H = 6·0; OMe = 10·3 per cent.

Calmatambetin is optically inactive. It is sparingly soluble in cold water, but readily so in alcohol or ethyl acetate, very sparingly so in ether, and insoluble in all the other usual organic solvents. It is insoluble in sodium carbonate solution, but dissolves readily in aqueous sodium hydroxide, giving a solution which assumes a sherry colour slowly in the cold, but quickly on boiling; this coloration is also produced on boiling with ferric chloride solution.

Calmatambetin reduces Fehling's solution. It is not precipitated by lead subacetate solution, and gives no coloration with cold concentrated nitric acid. It is converted into dark brown, resinous products when boiled with acetic anhydride either alone or with the addition of anhydrous sodium acetate or concentrated sulphuric acid. In the latter case, the addition of a drop of concentrated sulphuric acid to the solution of calmatambetin in boiling acetic anhydride produces a vivid carmine coloration which quickly changes to dark brown. An attempt to methylate calmatambetin by means of dimethyl sulphate produced only dark, resinous substances.

Action of Dilute Acids on Calmatambetin. Formation of a Substance, $C_{11}H_{12}O_3$.

Calmatambetin is very readily decomposed on boiling with dilute acids, but under suitable conditions a small quantity of a crystalline product could be isolated. Two and a half grams of calmatambetin were dissolved in 50 c.c. of 1 per cent. hydrochloric acid, and steam passed through the solution. The first litre of distillate was coloured yellow; it was neutral in reaction, and held in suspension a small amount of a scarlet, crystalline substance which was separated by filtration and set aside for analysis. A further small quantity of the substance was obtained by extraction of the distillate with ether, but the total yield only amounted to 4 per cent. of the weight of calmatambetin used. The residue consisted of a hard black resin from which no crystalline product could be obtained either directly or after fusion with potassium hydroxide at 160°.

The crystalline *substance*, which was separated from the distillate by filtration, melted at 91°. It was dried to constant weight in a vacuum :

0·0623 gave 0·1575 CO_2 and 0·0338 H_2O. C = 68·9 ; H = 6·1.
0·0430 ,, 0·1083 CO_2 ,, 0·0234 H_2O. C = 68·7 ; H = 6·1.
$C_{11}H_{12}O_3$ requires C = 68·7 ; H = 6·3 per cent.

The substance separates from ether in feathery needles, and has an aromatic odour. It is only slightly volatile with steam. It is very sparingly soluble in water, but very readily so in all the usual organic solvents. It is insoluble in acids or cold alkalis, but dissolves in boiling aqueous sodium hydroxide with a deep brown colour. It reduces Fehling's solution.

In conclusion, we wish to express our thanks to the Director of the Imperial Institute for suggesting the examination of the bark, and for a supply of raw material.

THE WELLCOME CHEMICAL WORKS.
DARTFORD, KENT.

CXIV.—*The Condensation of Aldehydes with Mixtures of α-Naphthol and α-Naphthylamine. Synthesis of 7-Aryl-*$\begin{array}{c}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{array}$*-dinaphthacridines.*

By Alfred Senier and Percy Corlett Austin.

In order to extend our knowledge of the dinaphthacridines, and particularly of $\begin{array}{c}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{array}$-dinaphthacridine (Trans., 1902, **81**, 288; 1906, **89**, 1390), we have studied the behaviour of formaldehyde and of alkyl and aryl aldehydes on mixtures of α- and β-naphthols and naphthylamines. We have made use of aldehydes, instead of the corresponding dihalides, which we have chiefly employed in previous work on acridines, because they were more easily procured. The use of α-naphthol and α-naphthylamine is a variation of a method which in the hands of Ullmann and Fetvadjian has given us the latest addition to the ranks of the typical dinaphthacridines (*Ber.*, 1903, **36**, 1027).

In a recent paper (*loc. cit.*), we described two $\begin{array}{c}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CR}'\text{–}\beta\end{array}$-dinaphthacridines, the 7-methyl and the 7-phenyl derivatives. To these should now be added the five bases described in this paper, all of which are derivatives of the same type.

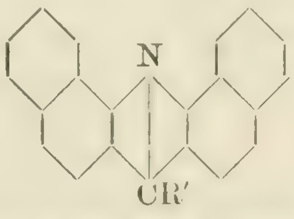
In the course of this and previous inquiries, our attention has been drawn to certain general differences between the dinaphthacridines of the $\begin{array}{c}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{array}$ (Senier and Goodwin) type on the one hand, and those of the $\begin{array}{c}\beta\text{–N–}\beta\\ |\\ \alpha\text{–CH–}\alpha\end{array}$ (Reed) type on the other. These differences are noticeable in the preparation of the bases: in their readiness or inability to form by condensation of aldehydes with naphthylamines and naphthols, and in the tendency in some cases to separate at once as bases and in others to form hydrides. Thus formaldehyde yields no dinaphthacridine with α-naphthylamine (Möhlau, *Ber.*, 1902, **35**, 4173), although Reed's base is obtained readily by the use of formaldehyde and β-naphthylamine.

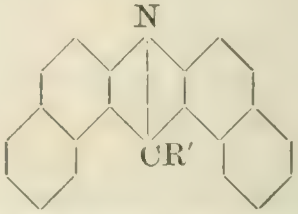
When methylene di-iodide or methylene dichloride is used, the difference is, however, not discernible, for with either dihalide both dinaphthacridines may be prepared (Trans., 1906, **89**, 1387). We have found by experiment that trioxymethylene has no action on a mixture of α-naphthylamine and α-naphthol, and that in this inability to condense, formaldehyde is joined by acetaldehyde and propaldehyde. On the other hand, with β-naphthylamine and β-naphthol (Ullmann and Fetvadjian, *Ber.*, 1903, 36, 1028), the corresponding dinaphthacridine is formed. Benzaldehyde yields both 7-phenyldinaphthacridines, but with other aryl aldehydes the difference becomes evident again. We have obtained the 7-aryl derivatives described below by condensing a mixture of α-naphthylamine and α-naphthol with the respective aldehydes, but were unable to induce a similar reaction to take place with β-naphthylamine and β-naphthol. Salicylaldehyde, *p*-hydroxybenzaldehyde, vanillin and piperonal showed no inclination to condense with naphthylamines and naphthols.

The tendency to form hydrides, observed by Morgan (Trans., 1898, 73, 536), Möhlau and Haase (*Ber.*, 1902, 35, 4169), Haase (*Ber.*, 1903, 36, 591), Ullmann and Fetvadjian (*Ber.*, 1903, 36, 1029), and Senier and Austin (Trans., 1906, 89, 1398), in the synthesis of $\begin{smallmatrix}\beta\text{–N–}\beta\\ |\\ \alpha\text{–CH–}\alpha\end{smallmatrix}$-dinaphthacridine is entirely absent in the case of the $\begin{smallmatrix}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{smallmatrix}$-isomeride, or of any of its derivatives.

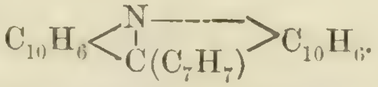
The differences described, which are shown in the synthetical formation of the $\begin{smallmatrix}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{smallmatrix}$ base on the one hand, and of the $\begin{smallmatrix}\beta\text{–N–}\beta\\ |\\ \alpha\text{–CH–}\alpha\end{smallmatrix}$ base on the other, may possibly be ascribed in part to steric influence, depending upon the position of the angular rings; compare Hinsberg on angular and linear ring formation (*Ber.*, 1903, 36, 4051).

When the angular rings can condense in the manner shown in the right-hand diagram (Reed's base), hydrides are formed, and condensation may be effected by formaldehyde and not by tolualdehyde or anisaldehydes, whilst when the angular rings can condense in the manner shown in the left-hand diagram (Senier and Goodwin's base), hydrides are not formed, and condensation is effected by tolu- and anisaldehydes and not by formaldehyde:



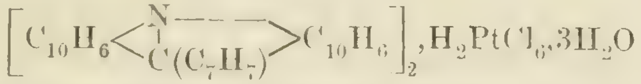


It may be noted that the phenomenon of triboluminescence is not observed in the case of any of the 7-aryl-$\begin{smallmatrix}\alpha\text{–N–}\alpha\\ |\\ \beta\text{–CH–}\beta\end{smallmatrix}$-dinaphthacridines described below, nor is it a character of the 7-methyl- or 7-phenyl-analogues, although the dinaphthacridine itself exhibits the phenomenon markedly.

7-o-Tolyl-$\begin{smallmatrix}\alpha-N-\alpha\\ |\\ \beta-CH-\beta\end{smallmatrix}$*-dinaphthacridine,* 
$C_{10}H_6<\begin{smallmatrix}N\text{———}\\ |\\ C(C_7H_7)\end{smallmatrix}>C_{10}H_6$.
—Twelve grams of α-naphthylamine and 12 grams of α-naphthol were heated together in a large test-tube; 5 grams of *o*-tolualdehyde were carefully added, a few drops at a time, and the mixture was well boiled after each addition of the aldehyde; finally the boiling was continued for a few minutes longer. After cooling, but before solidifying, the contents of the tube were poured into methylated spirit and allowed to stand until quite cold. The spirit was then decanted and the sticky residue treated with acetone until it was completely broken up into a yellow, crystalline powder. This was collected on a filter, washed with more acetone and then recrystallised once or twice from benzene. The base forms yellowish crystals, melting at 212° (215·5° corr.). It gives fluorescent solutions with benzene, toluene, glacial acetic acid, chloroform or carbon disulphide. In the two last-named solvents it is very easily soluble. Yield, 4—5 grams. On analysis:

0·1733 gave 0·5786 CO_2 and 0·0804 H_2O. C = 91·05; H = 5·15.
0·2182 gave 7·0 c.c. nitrogen at 15° and 757 mm. N = 3·74.
$C_{28}H_{19}N$ requires C = 91·05; H = 5·15; N = 3·79 per cent.

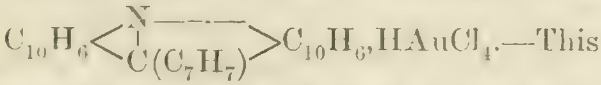
The following derivatives were prepared:

Platinichloride, 
$\left[C_{10}H_6<\begin{smallmatrix}N\text{———}\\ |\\ C(C_7H_7)\end{smallmatrix}>C_{10}H_6\right]_2,H_2PtCl_6,3H_2O$ (also with $2H_2O$).—A few drops of platinic chloride solution were added to a solution of the base in a mixture of glacial acetic and hydrochloric acids. The yellow precipitate which formed was washed with glacial acetic acid, then with dry ether, and dried in the desiccator and analysed:

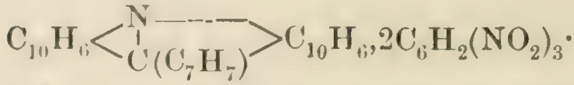
0·2618 gave 0·0425 Pt. Pt = 16·23.
$C_{56}H_{40}N_2Cl_6Pt,3H_2O$ requires Pt = 16·22 per cent.

Another portion was dried at 110° and analysed:

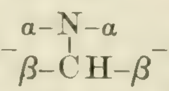
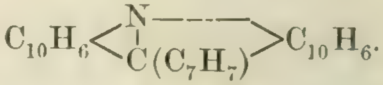
0·3633 gave 0·0596 Pt. Pt = 16·405.
$C_{56}H_{40}N_2Cl_6Pt,2H_2O$ requires Pt = 16·16 per cent.

Aurichloride, 
$C_{10}H_6<\begin{smallmatrix}N\text{———}\\ |\\ C(C_7H_7)\end{smallmatrix}>C_{10}H_6,HAuCl_4$.—This compound was obtained in orange crystals in the same manner as the platinichloride, but using gold chloride. After being washed with glacial acetic acid and dry ether and dried at 110°, it gave the following numbers on analysis:

0·3221 gave 0·0889 Au. Au = 27·60.
$C_{28}H_{20}NCl_4Au$ requires Au = 27·78 per cent.

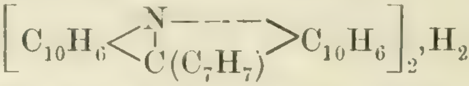
Picrate,  $C_{10}H_6<\begin{array}{c}N\\|\\C(C_7H_7)\end{array}>C_{10}H_6,2C_6H_2(NO_2)_3\cdot OH$.—Solutions of the base and of picric acid in the proportion of 2 mols. of the latter to one of the former were made in benzene, mixed and allowed to stand. A yellow crystalline precipitate soon formed, which was recrystallised from benzene and then from light petroleum. The compound is far more soluble in benzene than in petroleum. The crystals were dried at 105°, when they melted at 145° (147° corr.) to a reddish liquid.

0·1672 gave 0·3532 CO_2 and 0·0475 H_2O. C = 57·61 ; H = 3·15.
0·2282 gave 23·5 c.c. nitrogen at 14° and 748 mm. N = 11·92.
$C_{40}H_{25}O_{14}N_7$ requires C = 58·04. H = 3·02 ; N = 11·85 per cent.

7-m-*Tolyl*- $\begin{array}{c}\alpha-N-\alpha\\|\\\beta-CH-\beta\end{array}$-*dinapthacridine,*  $C_{10}H_6<\begin{array}{c}N\\|\\C(C_7H_7)\end{array}>C_{10}H_6$. —This compound was obtained in the same manner as the *o*-tolyl isomeride, using *m*-tolualdehyde instead of *o*-tolualdehyde. We obtained nearly 5 grams from 12 grams of *a*-naphthylamine, 12 grams of *a*-naphthol and 5 grams of the aldehyde. It dissolves in chloroform, benzene, toluene, and other organic solvents. On recrystallisation from benzene it melted at 251° (257° corr.).

0·2102 gave 0·7001 CO_2 and 0·0987 H_2O. C = 90·83 ; H = 5·21.
0·2518 ,, 8·6 c.c. nitrogen at 15·5° and 770 mm. N = 4·04.
$C_{28}H_{19}N$ requires C = 91·05 ; H = 5·15 ; N = 3·79 per cent.

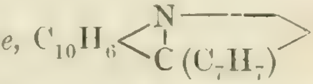
The following derivatives were prepared :

Platinichloride,  $\left[C_{10}H_6<\begin{array}{c}N\\|\\C(C_7H_7)\end{array}>C_{10}H_6\right]_2,H_2PtCl_6$ (also with $2H_2O$). —This was obtained as a yellow, crystalline precipitate by adding platinic chloride to a solution of the base in glacial acetic and hydrochloric acids. On drying in the desiccator :

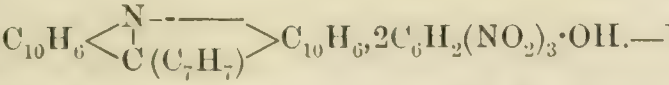
0·2046 gave 0·0335 Pt. Pt = 16·37.
$C_{56}H_{40}N_2Cl_6Pt,2H_2O$ requires Pt = 16·47 per cent.

On drying at 110° :

0·1976 gave 0·0335 Pt. Pt = 16·95.
$C_{56}H_{40}N_2Cl_6Pt$ requires Pt = 16·98 per cent.

Aurichloride,  $C_{10}H_6<\begin{array}{c}N\\|\\C(C_7H_7)\end{array}>C_{10}H_6,HAuCl_4$.—This was prepared from gold chloride in the same manner as that described for the platinichloride. It is a yellow, crystalline substance, and can be dried at 110°.

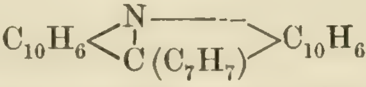
0·2621 gave 0·0725 Au. Au = 27·66.
$C_{28}H_{20}NCl_4Au$ requires Au = 27·78 per cent.



Picrate, $C_{10}H_6<\overset{N}{\underset{C(C_7H_7)}{|}}>C_{10}H_6,2C_6H_2(NO_2)_3\cdot OH$.—Yellow crystals of this compound were prepared by mixing benzene solutions of the base and of picric acid in the proportion of 1 molecule of the former to 2 of the latter. When recrystallised from benzene, the substance melts at 188° (191° corr.) to a clear red liquid.

0·1732 gave 17·1 c.c. nitrogen at 14·5° and 750 mm. N = 11·43.

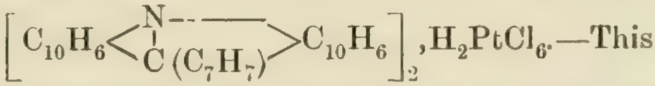
$C_{40}H_{25}O_{14}N_7$ requires N = 11·85 per cent.



7-p-*Tolyl*-$\overset{\alpha-N-\alpha}{\underset{\beta-CH-\beta}{|}}$-*dinaphthacridine,* $C_{10}H_6<\overset{N}{\underset{C(C_7H_7)}{|}}>C_{10}H_6$.—The preparation of this base was carried out in a similar way to that which gave the ortho- and meta-isomerides, *p*-tolualdehyde being used in this case. The base crystallises from benzene in pale greenish-yellow rhombohedra and melts at 221° (224° corr.). On analysis:

0·2246 gave 0·7495 CO_2 and 0·1070 H_2O. C = 91·01; H = 5·28.
0·2748 ,, 9·2 c.c. nitrogen at 11° and 761 mm. N = 3·96.

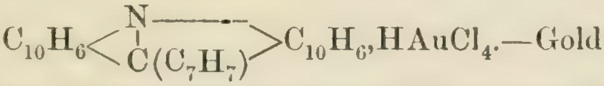
$C_{28}H_{19}N$ requires C = 91·05; H = 5·15; N = 3·79 per cent.



Platinichloride, $\left[C_{10}H_6<\overset{N}{\underset{C(C_7H_7)}{|}}>C_{10}H_6\right]_2,H_2PtCl_6$.—This is a yellow, crystalline compound, which, when dried at 110°, gave the following result on analysis:

0·3768 gave 0·0637 Pt. Pt = 16·905.

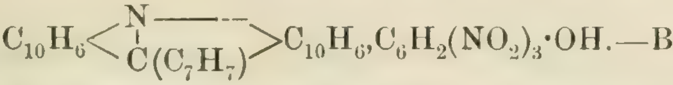
$C_{56}H_{40}N_2Cl_6Pt$ requires Pt = 16·98 per cent.



Aurichloride, $C_{10}H_6<\overset{N}{\underset{C(C_7H_7)}{|}}>C_{10}H_6,HAuCl_4$.—Gold chloride united with the base to form orange crystals of the above composition. They were dried at 110° and analysed:

0·2296 gave 0·0632 Au. Au = 27·52.

$C_{28}H_{20}NCl_4Au$ requires Au = 27·78 per cent.

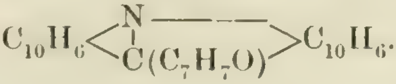


Picrate, $C_{10}H_6<\overset{N}{\underset{C(C_7H_7)}{|}}>C_{10}H_6,C_6H_2(NO_2)_3\cdot OH$.—By mixing hot solutions of the base and of picric acid in equimolecular proportions, a slightly reddish liquid was obtained which on cooling deposited yellow crystals. These were recrystallised from a mixture of benzene and light petroleum, washed with the same mixture and dried at 110°. The melting point is 229° (234° corr.). On analysis:

0·2470 gave 20·4 c.c. nitrogen at 13·5° and 760 mm. N = 9·74.

$C_{34}H_{22}O_7N_4$ requires N = 9·37 per cent.

7-p-*Methoxyphenyl*- (*anisyl*-) $\overset{\alpha-N-\alpha}{\underset{\beta-CH-\beta}{|}}$-*dinaphthacridine,*



$C_{10}H_6<\overset{N}{\underset{C(C_7H_7O)}{|}}>C_{10}H_6$.

—This compound was formed by treating a boiling mixture of α-naphthylamine and α-naphthol with anisaldehyde. The warm product was poured into methylated spirit and cooled; the spirit was then decanted, and the residue treated with acetone and collected on a filter. When recrystallised from benzene, it separated in clusters of small, yellow rhombohedra, melting at 257° (263° corr.). Using 13 grams of α-naphthylamine, 13 grams of α-naphthol, and 12 grams of anisaldehyde, we obtained 7—8 grams of the dinapthacridine:

0·1845 gave 0·5896 CO_2 and 0·0863 H_2O. C = 87·15; H = 5·19.
0·2588 „ 8·0 c.c. nitrogen at 11° and 767 mm. N = 3·72.
$C_{28}H_{19}ON$ requires C = 87·27; H = 4·93; N = 3·63 per cent.

The following derivatives were examined:

Platinichloride, $\left[C_{10}H_6<\overset{N}{\underset{C(C_7H_7O)}{|}}>C_{10}H_6\right]_2,H_2PtCl_6,3H_2O$ (also with $2H_2O$).—A solution of platinic chloride, added to a solution of the base in glacial acetic acid mixed with hydrochloric acid, gave a precipitate of orange crystals, which after being washed with dry ether and allowed to stand for several hours in the desiccator, gave the following figures on analysis:

0·3185 gave 0·0503 Pt. Pt = 15·79.
$C_{56}H_{40}O_2N_2Cl_6Pt,3H_2O$ requires Pt = 15·79 per cent.

By drying at 110°, one molecule of water is driven off:

0·3577 gave 0·0575 Pt. Pt = 16·07.
$C_{56}H_{40}O_2N_2Cl_6Pt,2H_2O$ requires Pt = 16·03 per cent.

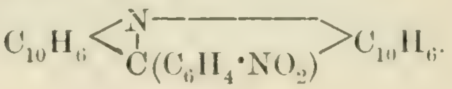
Aurichloride, $C_{10}H_6<\overset{N}{\underset{C(C_7H_7O)}{|}}>C_{10}H_6,HAuCl_4$.—This is obtained as a yellow precipitate when gold chloride is used instead of platinic chloride. After being washed with dry ether and dried at 110°, it gave the following result on analysis:

0·3526 gave 0·0952 Au. Au = 26·999.
$C_{28}H_{20}ONCl_4Au$ requires Au = 27·17 per cent.

Picrate, $C_{10}H_6<\overset{N}{\underset{C(C_7H_7O)}{|}}>C_{10}H_6,2C_6H_2(NO_2)_3\cdot OH$.—When solutions of the base (1 mol.) and of picric acid (2 mols.) in benzene were heated and mixed, a red liquid was obtained, which on cooling deposited orange crystals. These were recrystallised from benzene, when they melted at 192°.

0·1350 gave 13·4 c.c. nitrogen at 17° and 764 mm. N = 11·58.
$C_{40}H_{25}O_{15}N_7$ requires N = 11·62 per cent.

7-m-*Nitrophenyl*-$\overset{\alpha-N-\alpha}{\underset{\beta-CH-\beta}{|}}$-*dinaphthacridine*,

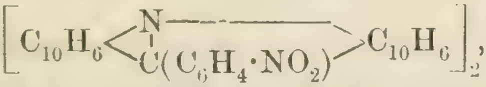


$$C_{10}H_6<\overset{N}{\underset{C(C_6H_4\cdot NO_2)}{|}}>C_{10}H_6.$$

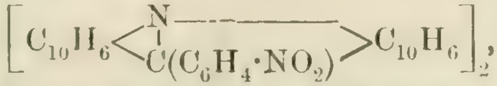
—In the preparation of this base, more careful heating was found to be necessary than was the case with any of the preceding dinaphthacridines, otherwise the reaction became too violent and the mass charred. The best results were obtained by preparing small quantities at a time. Five grams of α-naphthylamine and 5 grams of α-naphthol were melted together and heated to boiling; 2 grams of the solid *m*-nitrobenzaldehyde were added gradually and the heating discontinued until all had been added. The mixture was finally heated for about one minute over the free flame. More prolonged heating caused the liquid to become rapidly darker, an indication that decomposition was beginning. While still hot it was carefully poured into a porcelain dish, and, when sufficiently cool, ethyl acetate or acetone was added. On standing, yellow crystals of the base separated. The substance is almost insoluble in glacial acetic acid, and is less soluble in benzene, toluene, &c., than the other dinaphthacridines described. No sign of fluorescence was observed in the solutions. It was recrystallised from benzene, but did not melt below 300°. On analysis:

0·1657 gave 0·4956 CO_2 and 0·0626 H_2O. C = 81·57; H = 4·13.
0·1540 ,, 9·6 c.c. nitrogen at 17° and 748·5 mm. N = 7·12.
$C_{27}H_{16}O_2N_2$ requires C = 81·00; H = 4·00; N = 7·00 per cent.

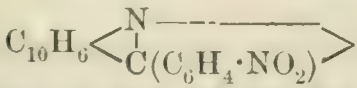
We prepared the following derivatives:

Platinichloride,  $\left[C_{10}H_6<\begin{matrix}N\text{———————}\\ |\\ C(C_6H_4\cdot NO_2)\end{matrix}>C_{10}H_6\right]_2,H_2PtCl_6$.—Although the base is practically insoluble in glacial acetic acid, it is rendered very soluble by adding a few drops of concentrated hydrochloric acid to the glacial acetic acid. A few drops of platinic chloride added to this solution produced a yellow, crystalline precipitate, which was washed with dry ether, then dried at 105° and analysed:

0·2354 gave 0·0382 Pt. Pt = 16·22.
$C_{54}H_{34}O_4N_4Cl_6Pt$ requires Pt = 16·11 per cent.

Aurichloride,  $\left[C_{10}H_6<\begin{matrix}N\text{———————}\\ |\\ C(C_6H_4\cdot NO_2)\end{matrix}>C_{10}H_6\right]_2,HAuCl_4$.—Orange crystals of the gold salt were obtained by using gold chloride instead of platinic chloride. They were washed with dry ether and dried at 110°.

0·1612 gave 0·0278 Au. Au = 17·24.
$C_{54}H_{33}O_4N_4Cl_4Au$ requires Au = 17·28 per cent.

Picrate,  $C_{10}H_6<\begin{matrix}N\text{———————}\\ |\\ C(C_6H_4\cdot NO_2)\end{matrix}>C_{10}H_6,2C_6H_2(NO_2)_3\cdot OH$.—Hot solutions of the base (1 mol.) and of picric acid (2 mols.) in benzene were mixed. As nothing separated on cooling, light petroleum was added until a slight cloudiness was produced. On rubbing, a yellow, flaky precipitate soon appeared. This was washed on the filter with light petroleum and dried at 105°. It melted at 160° (162·5° corr.).

0·1350 gave 15·3 c.c. nitrogen at 15° and 755 mm. N = 13·18.

$C_{39}H_{22}O_{16}N_8$ requires N = 13·05 per cent.

QUEEN'S COLLEGE,
GALWAY.

CXV.—*The Synthesis of Phenonaphthacridines: Trimethylphenonaphthacridines.*

By ALFRED SENIER and PERCY CORLETT AUSTIN.

THE experiments described in this paper were undertaken in order to determine whether the methylene di-iodide and arylamine method (Senier and Goodwin, Trans., 1902, **81**, 280) could be applied to the synthesis of phenonaphthacridines. For this purpose we tried to effect condensations with methylene di-iodide, using ψ-cumidine and α-naphthylamine, and ψ-cumidine and β-naphthylamine. In the experiments with α-naphthylamine, $\begin{matrix}\alpha-N-\alpha\\ \vert\\ \beta-CH-\beta\end{matrix}$-dinaphthacridine is formed with a small and uncertain proportion of trimethylphenonaphthacridine, whilst in those with β-naphthylamine no trace of a phenonaphthacridine could be detected, but a mixture of 1 : 3 : 4 : 6 : 7 : 9-hexamethylacridine (Senier and Goodwin, Trans., *loc. cit.*) and either $\begin{matrix}\beta-N-\beta\\ \vert\\ \alpha-CH-\alpha\end{matrix}$-dinaphthacridine or bis-$\begin{matrix}\beta-N-\beta\\ \vert\\ \alpha-CH-\alpha\end{matrix}$-dinaphthacridine dihydride was obtained.

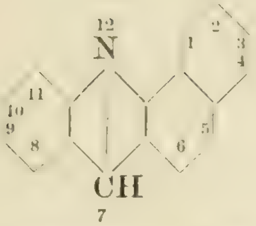
In order to prevent the formation of dinaphthacridines, α- and β-naphthols were then substituted for the corresponding naphthylamines, with the result that the condensation we desired was effected, and the two trimethylphenonaphthacridines, the one derived from α- and the other from β-naphthol, were readily obtained in a state of purity. We also took advantage of the reaction between formaldehyde and a mixture of an arylamine and a naphthol, which Ullmann and his co-workers have so successfully applied in the synthesis of phenonaphthacridines. This method gave us the same bases, but the yields were small and the substances were difficult to purify.

Three isomeric phenonaphthacridines are theoretically possible (Senier, *Brit. Assoc. Report*, 1903, 616; *Chem. News*, 1903, **88**, 296;

Ullmann and La Torre, *Ber.*, 1904, **37**, 2922). All three are now known.

One is N–*α*.

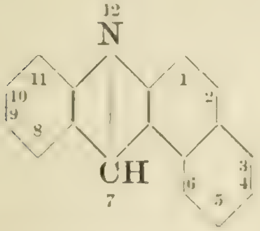
A.



Ullmann and La Torre.

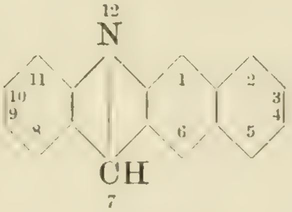
Two are N–*β*.

B.



Ullmann and Nalband.

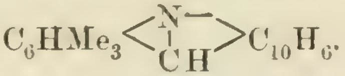
C.



Schöpff.

The bases described below are of the types *A* and *B*. The notation adopted is that proposed by one of us (*Brit. Assoc. Report*), and the numbering is in accordance with that suggested in a previous paper for dinaphthacridines (Trans., 1906, **89**, 1387).

I. 8 : 9 : 11-*Trimethylpheno*-$\overset{\text{N}-\alpha}{\underset{\text{CH}-\beta}{|}}$-*naphthacridine.**



$$C_6HMe_3\!<\!\!\overset{\text{N}—}{\underset{\text{CH}}{|}}\!\!>\!C_{10}H_6.$$

ψ-Cumidine (2 mols.) and *α*-naphthol (2 mols.) were melted and heated to boiling in a large test-tube, and methylene di-iodide (1 mol.) was added drop by drop. The boiling was continued for several minutes, after which the mixture was allowed to cool. The resulting solid, which consisted of a rather unstable salt of the phenonaphthacridine, was then warmed for a few minutes with a little alcoholic ammonia. The base was thereby liberated, and when collected on a filter and washed with acetone was nearly pure. It was recrystallised once or twice from benzene, from which it separated in greenish-yellow crystals melting at 160° (162·5° corr.). It may also be recrystallised from glacial acetic acid or ethyl acetate. It is almost insoluble in cold glacial acetic acid, but readily soluble in hot, resembling in this point hexamethylacridine. All these solutions are fluorescent. On analysis:

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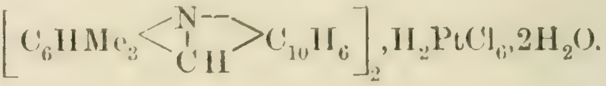
* According to Ullmann and Naef (*Ber.*, 1900, **33**, 907), the designation of this compound would be 1′ : 2′ : 4′-trimethyl-2 : 1-naphthacridine.

0·1762 gave 0·5740 CO_2 and 0·1062 H_2O. C = 88·84; H = 6·69.
0·2428 „ 10·9 c.c. nitrogen at 16·5° and 770 mm. N = 5·29.
$C_{20}H_{17}N$ requires C = 88·56; H = 6·27; N = 5·16 per cent.

The following derivatives were prepared:

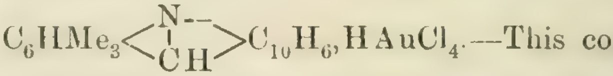
Platinichloride,



$\left[C_6HMe_3{<}\overset{N-\!-}{\underset{CH}{|}}{>}C_{10}H_6\right]_2,H_2PtCl_6,2H_2O.$

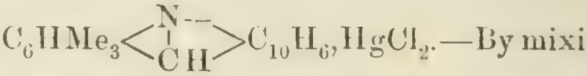
Orange crystals of this compound were obtained by adding a few drops of platinic chloride solution to a solution of the base in glacial acetic acid mixed with hydrochloric acid. After being washed with dry ether and dried at 105°, they gave the following figures on analysis:

0·2680 gave 0·0528 Pt. Pt = 19·701.
$C_{40}H_{40}O_2N_2Cl_6Pt$ requires Pt = 19·72 per cent.



Aurichloride, $C_6HMe_3{<}\overset{N-\!-}{\underset{CH}{|}}{>}C_{10}H_6,HAuCl_4$.—This compound was prepared by treating a solution of the base in glacial acetic acid containing hydrochloric acid with a few drops of gold chloride solution. It formed orange crystals which were washed with dry ether and dried at 110°.

0·2206 gave 0·0696 Au. Au = 31·77.
$C_{20}H_{18}NCl_4Au$ requires Au = 32·27 per cent.

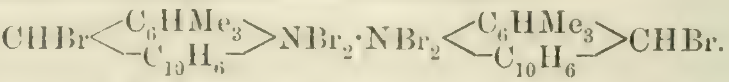


Mercurichloride, $C_6HMe_3{<}\overset{N-\!-}{\underset{CH}{|}}{>}C_{10}H_6,HgCl_2$.—By mixing solutions of the base and of mercuric chloride in glacial acetic acid mixed with hydrochloric acid a yellow precipitate was formed. After recrystallisation from the same solvent it was washed with dry ether and dried at 105°. It melted between 260° and 263° to a red liquid. On analysis:

0·2915 gave 0·1207 HgS. Hg = 35·69.
$C_{20}H_{17}NCl_2Hg$ requires Hg = 36·90 per cent.

The specimen was evidently not quite pure.

Bistrimethylphenonaphthacridine hexabromide,



$CHBr{<}\begin{matrix}C_6HMe_3\\-C_{10}H_6-\end{matrix}{>}NBr_2\cdot NBr_2{<}\begin{matrix}C_6HMe_3\\-C_{10}H_6-\end{matrix}{>}CHBr.$

This compound, which is analogous to the diacridine hexahalides described by us in a previous paper (Trans., 1904, **85**, 1202), was obtained as an orange-yellow precipitate by adding excess of a warm solution of bromine in glacial acetic acid to a solution of the base in a mixture of glacial acetic acid and benzene. The crystals were washed with dried ether and dried at 110°. On analysis:

0·1577 gave 0·1720 AgBr. Br = 46·408.

$C_{40}H_{34}N_2Br_6$ requires Br = 46·96 per cent.

Picrate, $C_6HMe_3<\substack{N--\\ |\\ CH}>C_{10}H_6,C_6H_2(NO_2)_3\cdot OH$.—When warm solutions in benzene of the base and of picric acid in equimolecular proportions were mixed and allowed to cool, orange crystals of the picrate separated. On recrystallising from benzene, washing with light petroleum and drying at 105°, they melted at 170° (172° corr.).

0·1438 gave 13·8 c.c. nitrogen at 15° and 766 mm. N = 11·33.

$C_{26}H_{20}O_7N_4$ requires N = 11·20 per cent.

A somewhat too vigorous reaction is induced when α-naphthylamine, ψ-cumidine, and methylene di-iodide are heated together. This may be modified by adding to the mixture powdered potassium carbonate and a little benzene and heating in a sealed tube to 200°. The resulting product appears, however, to be a mixture in uncertain proportions of $\substack{\alpha-N-\alpha\\ |\\ \beta-CH-\beta}$-dinaphthacridine and of the trimethylpheno-$\substack{N-\alpha\\ |\\ CH-\beta}$-naphthacridine, a mixture which is not easily separated into its two components. When alkali was used we found that the phenonaphthacridine preponderated, but owing to the difficulty of getting it to crystallise, the yield was very small. Several experiments were made without the use of alkali, and in one of these we obtained only the dinaphthacridine, whilst in others a yellow solid was obtained which dissolved readily in chloroform, carbon disulphide, benzene, toluene, or ethyl acetate, less readily in light petroleum, and only sparingly in alcohol, but in no case did well-formed crystals separate. By repeated crystallisation, however, we were able to obtain two different solids, both evidently impure, one of which melted a few degrees below the melting point of trimethylpheno-$\substack{N-\alpha\\ |\\ CH-\beta}$-naphthacridine and the other melted near the melting point of $\substack{\alpha-N-\alpha\\ |\\ \beta-CH-\beta}$-dinaphthacridine. In no case could any indication of the formation of hexamethylacridine be found.

The preparation of this base was also effected by Ullmann's method. Equimolecular proportions of α-naphthol and ψ-cumidine were boiled together in a test-tube. Paraformaldehyde (1 mol. to 1 mol. of ψ-cumidine) was added in small portions and the resulting mass boiled until most of the frothing had disappeared. The mixture was then poured into warm dilute potassium hydroxide, when it formed a viscid oil, which soon solidified. It was washed successively with water and alcohol, but gave on crystallisation from ethyl acetate only a small yield of the phenonaphthacridine.

II. 8 : 9 : 11-*Trimethylpheno*-$\begin{matrix}N-\beta\\ |\\ CH-\alpha\end{matrix}$-*naphthacridine.**

$$C_6HMe_3<\begin{matrix}N--\\ |\\ CH\end{matrix}>C_{10}H_6.$$

Nine grams of ψ-cumidine were melted with 10 grams of β-naphthol, and the liquid heated to boiling. Five grams of methylene di-iodide were gradually added, and the boiling continued for five or ten minutes. The hot liquid was then poured into a porcelain dish, and when cold treated with ethyl acetate and allowed to stand. An orange-yellow compound separated, which was freed from the mother-liquor by filtration. This compound, which contained iodine, was only slightly soluble in benzene, toluene, glacial acetic acid or ethyl acetate, somewhat more so in alcohol, but readily soluble in hot aniline, from which it crystallised, on cooling, in orange needles. On analysis this substance proved to be the hydriodide of the trimethylphenonaphthacridine. For the preparation of the latter, the hydriodide was dissolved, without previous recrystallisation from aniline, in methylated spirit, to which was added a little concentrated ammonium hydroxide. This solution, when filtered and cooled, deposited pale yellow needles of trimethylpheno-$\begin{matrix}N-\beta\\ |\\ CH-\alpha\end{matrix}$-naphthacridine. In order to obtain a specimen sufficiently pure for analysis, it was recrystallised from alcohol. It is much more soluble in benzene, toluene, or glacial acetic acid than its isomeride, described above. It also dissolves readily in acetone, ether, or ethyl acetate, but crystallises best from absolute alcohol or methylated spirit in fine straw-coloured needles, melting at 136° (137° corr.). The solutions are very faintly fluorescent.

0·1378 gave 0·4479 CO_2 and 0·0796 H_2O. C = 88·64 ; H = 6·41.
0·1670 gave 7·4 c.c. nitrogen at 17° and 765 mm. N = 5·17.
$C_{20}H_{17}N$ requires C = 88·56 ; H = 6·27 ; N = 5·16 per cent.

The following derivatives were examined:

Hydriodide, $C_6HMe_3<\begin{matrix}N--\\ |\\ CH\end{matrix}>C_{10}H_6,HI$.—This salt, which was obtained as an intermediate product in the preparation of the base, as described above, was recrystallised from aniline, washed with dry ether, and dried at 110°. It forms orange crystals, which do not melt below 300°.

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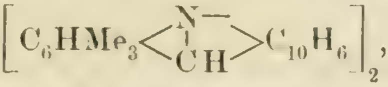
* 1′ : 2′ : 4′-Trimethyl-1 : 2-naphthacridine according to the notation of Ullmann and Naef.

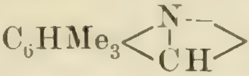
0·1476 gave 0·0872 AgI. I = 31·92.

$C_{20}H_{18}NI$ requires I = 31·83 per cent.

Platinichloride,  $\left[C_6HMe_3<\begin{matrix}N-\\|\\CH\end{matrix}>C_{10}H_6\right]_2, H_2PtCl_6$.—The platinum salt was precipitated as a yellow powder when a few drops of platinic chloride were added to a solution of the base in glacial acetic acid. After being washed on a filter with dry ether and dried at 110°, it gave the following figures on analysis :

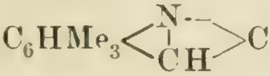
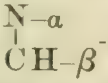
0·1216 gave 0·0248 Pt. Pt = 20·39.

$C_{40}H_{36}N_2Cl_6Pt$ requires Pt = 20·47 per cent.

Aurichloride,  $C_6HMe_3<\begin{matrix}N-\\|\\CH\end{matrix}>C_{10}H_6,HAuCl_4$.—A yellow precipitate separated on adding a few drops of gold chloride to a solution of the base in glacial acetic acid. This precipitate was washed with dry ether and dried at 110°. On analysis :

0·1449 gave 0·0466 Au. Au = 32·16.

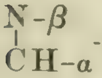
$C_{20}H_{18}NCl_4Au$ requires Au = 32·27 per cent.

Picrate,  $C_6HMe_3<\begin{matrix}N-\\|\\CH\end{matrix}>C_{10}H_6,C_6H_2(NO_2)_3\cdot OH$.—This derivative was obtained as a yellow precipitate when equimolecular solutions of the base and of picric acid in benzene were mixed. The analysis shows that it is isomeric with the corresponding derivative of trimethylpheno-  $\begin{matrix}N-\alpha\\|\\CH-\beta\end{matrix}$ -naphthacridine, but unlike the latter it is almost insoluble in benzene. As no suitable solvent could be found for recrystallising this substance, it was simply washed with a little benzene and light petroleum, and dried at 105°. It has no sharp melting point, but begins to decompose at about 262°.

0·1251 gave 0·2851 CO_2 and 0·0520 H_2O. C = 62·15 ; H = 4·61.

0·1119 gave 11·4 c.c. nitrogen at 15·5° and 756 mm. N = 11·84.

$C_{26}H_{20}O_7N_4$ requires C = 62·40 ; H = 4·00 ; N = 11·20 per cent.

In the next place we investigated the reaction which takes place when ψ-cumidine, β-naphthylamine and methylene di-iodide are heated together. It differs in character from the corresponding reaction with α-naphthylamine, for no trace of the trimethylpheno-  $\begin{matrix}N-\beta\\|\\CH-\alpha\end{matrix}$ -naphthacridine could be found. When equimolecular proportions of ψ-cumidine, β-naphthylamine and methylene di-iodide were heated together with or without potassium carbonate in an open flask in an oil-bath at 180°, the resulting solid was a mixture of hexamethylacridine and Reed's $\begin{array}{c}\beta\text{–N–}\beta\\ |\\ \alpha\text{–CH–}\alpha\end{array}$-dinaphthacridine.* When heated in a sealed tube to 200° we obtained hexamethylacridine and bis-$\begin{array}{c}\beta\text{–N–}\beta\\ |\\ \alpha\text{–CH–}\alpha\end{array}$-dinaphthacridine dihydride (Morgan's "*iso*naphthacridine").

Using Ullmann's method we obtained trimethylpheno-$\begin{array}{c}\text{N–}\beta\\ |\\ \text{CH–}\alpha\end{array}$-naphthacridine, but the yield was small and the product was not easily purified. Paraformaldehyde was added to a heated mixture of β-naphthol and ψ-cumidine in the usual way, and the heating continued until most of the frothing had ceased. The liquid, after cooling slightly, was poured into warm aqueous potassium hydroxide, and the solid residue was washed with water and with alcohol. It was then crushed and washed with a little ethyl acetate. The washed solid on recrystallising from toluene gave crystals melting at 137—140°. On dissolving in acetone and fractionating by crystallisation, two substances were separated, one melting at about 180—182°, but occurring only in very small proportion, and the other (more soluble) melting at 135—136°. The latter proved to be trimethylpheno-$\begin{array}{c}\text{N–}\beta\\ |\\ \text{CH–}\alpha\end{array}$-naphthacridine. The substance with the higher melting point was not further examined, as only a very small portion was obtained.

QUEEN'S COLLEGE,
GALWAY.

CXVI.—*The Affinity Constants of Aminosulphonic Acids as Determined by the Aid of Methyl-Orange.*

By VICTOR HERBERT VELEY.

IN former papers (*Zeitsch. physikal. Chem.*, 1906, **57**, 147, and Trans., 1907, **91**, 153) it was shown that (i) the affinity constants as determined by the above method conform either to a logarithmic type ($\log y = \log k + x \log a$) or to a straight-line type $y = kx$, and (ii) in the particular case of the naphthylaminesulphonic acids the positions 2 and, to a less extent, 7 afford cases of steric "furtherance," whilst the position 8 affords a case of steric "hindrance." It was thought worthy of interest to pursue the latter subject with reference to the aminonaphtholsulphonic acids, more especially as regards the effect produced by the introduction of the hydroxyl group in different relative positions to the sulphonic acid group. So far as I am aware, no results have been obtained by the electric conductivity method for the aminonaphtholsulphonic acids, mainly owing to the experimental difficulties of obtaining these compounds in a reasonable degree of purity, and their sparing solubility.

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* For this experiment we are indebted to Miss F. M. G. Micklethwait, who conducted it in connexion with other acridine work a few years ago.

Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 170 *et seq.*) has shown that the effect produced by the introduction of the hydroxyl group on the benzenoid carboxylic acids varies greatly according to the position taken up by the hydroxyl.

While my former papers were in the press, an investigation on various indicators was published by Salm (*Zeitsch. physikal. Chem.*, 1906, **57**, 471); certain results were obtained by the tintometer method with methyl-orange. Although the form of experiment used was not identical with that adopted by me, yet the same practical conclusions follow as a consequence of both lines of research, namely, that "it is necessary in volumetric analysis to titrate to one constant tint, which corresponds to a known concentration of hydrogen ions," more especially in the cases of two-coloured indicators.

It is again my pleasant duty to express my obligations to the Directors of the Badische Anilin- und Soda-Fabrik for supplying me with the necessary materials.

Aminonaphtholsulphonic Acids.

It was not found practicable to purify these acids by recrystallisation, partly owing to their sparing solubility, and partly to the tendency of carbonaceous matters to separate out when the solutions were evaporated under the ordinary pressure. The following method was therefore adopted; molecular equivalents of the several acids in centigrams were suspended in 25 c.c. of water, then a quantity of *N*-sodium carbonate solution added in slight excess of that required to neutralise the acid. The mixture was warmed until the acid had passed into solution and all the carbon dioxide was apparently displaced. It was observed that the rapidity with which the several acids decomposed the sodium carbonate differed widely under approximately similar conditions, but the problem of the relative affinities of the sodium ion for the aminonaphtholsulphonic and the carbonic ions, although interesting in itself, was beyond the sphere of this investigation.

The solutions obtained in this way were filtered, and then *N*-sulphuric acid added in a quantity slightly less than that of the *N*-sodium carbonate originally taken. The acids were thus reprecipitated as amorphous powders, which were washed, and dried at 25°; they were thus obtained as powders either white or of a pale pink or green tint. Solutions were made up of $N/400$, $N/200$ or $N/100$ concentrations according to circumstances, and these were in some cases slightly above or below the saturation point at the ordinary temperature. It may be worth remarking incidentally that the introduction of the hydroxyl group in the naphthylaminesulphonic acids almost completely extinguishes their remarkable fluorescence. The methods of working and of calculating the results are identical with those of my former papers on the same subject.

5-*Amino*-1-*naphthol*-3-*sulphonic acid*,* obtained in pale pink solution, was kept slightly warm to prevent recrystallisation.

TABLE I.

$V = 8 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·4	0·55	1·0	1·25
1·1	1·1	2·4	2·5
2·2	2·2	5·0	5·0
—	—	9·9	10·0

The values in the second and fourth columns are calculated from the expression $\log y = \log k + x \log a$ (k = 0·55 and 1·25, a = 2 respectively).

The above values are identical within the limit of experimental error with those obtained for the 1-naphthylamine-7-sulphonic acid, thus showing that the introduction of the hydroxyl group in a meta-position relative to the sulphonic acid group produces no alteration in the affinity constant. This result is precisely analogous to that found by Ostwald for *m*-hydroxybenzoic acid as compared with benzoic acid.

8-*Amino*-1-*naphthol*-4-*sulphonic acid* was obtained as a pale violet solution.

TABLE II.

$V = 4 \times 10^4$.	
y (found).	y (calc.).
0·3	0·35
0·8	0·7
1·6	1·4
2·8	2·8

On comparison of the above results with those obtained for the 1-naphthylamine-5-sulphonic acid, it appears that the introduction of the hydroxyl group in the 8-position reduces the affinity constant to about one-third of its value (actually 1·12 to 0·35). This result appears to afford a case of steric hindrance caused by the introduction of the hydroxyl group in the 8-position; it is also analogous with the results obtained both by Ostwald and myself, which show that the introduction of the hydroxyl group in the 4-position relative to the carboxyl produces a considerable diminution (50—60 per cent.) in the affinity constant.

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* In order to make the arguments intelligible, it will be understood that in my former paper the naphthylaminesulphonic acids were considered as derived from α- and β-naphthylamine; in the present paper, the aminonaphtholsulphonic acids are considered as derived from α- and β-naphthol. The numbering of the groupings is thereby altered, but not their relative positions.

8-*Amino*-1-*naphthol*-5-*sulphonic acid* gave an almost colourless solution, which was kept warm to prevent crystallisation:

TABLE III

$V = 8 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
1	0·9	1·8	2·05
2·2	1·8	4·0	4·1
3·8	3·6	7·8	8·2
7·0	7·2	16·6	16·4

The values in the second and fourth columns are calculated from the expression $\log y = \log k + x \log a$ ($k = 0·9$ and $2·05$, $a = 2$ respectively).

In this case no comparison is possible with the 1-naphthylamine-4-sulphonic acid, which was found to be not sufficiently soluble for observations.

6-*Amino*-2-*naphthol*-4-*sulphonic acid* was obtained as a pale pink solution.

TABLE IV.

$V = 4 \times 10^4$.		$V = 2 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
2·2	2·2	4·1	4·3
4·2	4·4	8·4	8·6
6·2	6·6	12·8	12·9
8·6	8·8	17·4	17·2
10·8	11·0	22·0	21·5
13·6	13·2	—	—
16·4	15·4	—	—

The values in the second and fourth columns are calculated from the straight-line formula $y = kx$ ($k = 2·2$ and $4·3$ respectively), but it will be observed that although the differences $y^1 - y$ are at first constant, there is a tendency for this difference to increase, as previously observed in the cases of salicylic and oxanilic acids, &c.

The introduction of the hydroxyl group in the 6-position increases the affinity constant, as the 2-naphthylamine-8-sulphonic acid was found to be inert.

This result is not in accordance with those obtained for the 1-naphthylamine-7-sulphonic acid and 5-amino-1-naphthol-3-sulphonic acid (p. 1248), and it would thus appear that in the case of naphthalene the positions 5 : 7 and 6 : 8 are not the same relative to 1 and 2 or to one another. It is further remarkable, on comparing 2-naphthylamine-6 : 8-disulphonic acid and 6-amino-2-naphthol-4-sulphonic acid, that the substitution of the sulphonic group in the former by the hydroxyl group should increase the affinity constant from *nil* to a considerable value. There does not appear to be any data of analogous cases available for the purpose of comparison, so further speculation in the present state of knowledge seems undesirable.

6-*Amino*-1-*naphthol*-3-*sulphonic acid* was obtained in nearly colourless solution, and kept slightly above the ordinary temperature for the purpose of observation.

TABLE V.

$V = 4 \times 10^4$.

y (found).	y (calc.).
1	1
2	2
3	3
4	4
4·9	5

These results are also in accordance with the straight-line formula $k = 1$; on comparison with those obtained for 2-naphthylamine-7-sulphonic acid, it appears that the end point is nearly the same (4·6 and 4·9), although arrived at by different stages of the logarithmic and straight-line types.

The general net result is that the introduction of the hydroxyl group in the meta-position produces only a slight alteration in the affinity constant (see p. 1248 as to comparison of 1-naphthylamine-7-sulphonic acid and 5-amino-1-naphthol-3-sulphonic acid).

8-*Amino*-1-*naphthol*-3 : 6-*disulphonic acid* could not be purified by the method used for the mono-acids, so that it was examined directly, the solution being of a pink colour.

TABLE VI.

$V = 4 \times 10^4$.

y (found).	y (calc.).
0·6	0·65
1·2	1·3
2·8	2·6
5·4	5·2

The value of $k = 0·65$ and $a = 2$.

It is not possible to draw any conclusion as to the effect of the introduction of the hydroxyl group in the 8-position, as the 1-naphthylamine-3 : 6-disulphonic acid has not been examined.

Naphtholsulphonic Acids.

Attempts were made to obtain solutions of these acids, fit for investigation, by precipitating their sodium or potassium salts with basic lead acetate, and then decomposing the lead salts suspended in water by a current of hydrogen sulphide. The excess of dissolved gas in the filtered solution was driven off by warming partly at ordinary and partly at reduced pressure. But although the solutions obtained in this way contained abundance of acid as shown by titration with a $N/10$-soda solution, phenolphthalein being used as an indicator, it was not found possible to obtain satisfactory observations by the methyl-orange tintometer method, as the orange-red tint produced at first by addition of successive quantities of the acid solution disappeared more or less quickly, doubtless owing to some secondary change. The investigation of this series of acids was therefore reluctantly abandoned.

Summary.

(I) The affinity constants of the aminonaphtholsulphonic acids, as determined by the methyl-orange tintometer method, show, as regards the effect of the introduction of the hydroxyl group in the naphthylaminesulphonic acids, relationships similar to those observed by Ostwald by the electric conductivity method for the hydroxybenzoic acids as compared with benzoic acid.

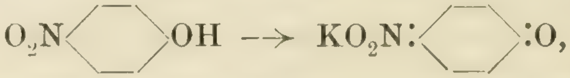
(II) One possible case of steric hindrance induced by the introduction of the hydroxyl group in the 8-position is noted.

I desire to express my thanks to Mr. J. E. Marsh, F.R.S., for practical assistance and suggestions.

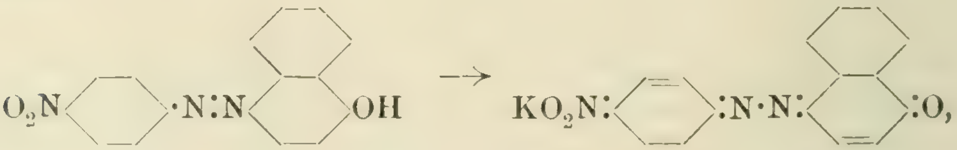
CXVII.—*Colour and Constitution of Azo-compounds. Part I.*

By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

IN two papers brought before the Society rather more than a year ago (Trans., 1906, **89**, 13, 17) attention was drawn to the remarkable change of colour observed when *p*-nitrobenzeneazo-4 : 6-dimethylcoumarin and *p*-nitrobenzeneazo-4-methyl-α-naphthacoumarin were dissolved in alkali. Both substances are reddish-brown in colour and they dissolve in neutral solvents with a similar shade; the former gives, however, a violet solution in alkali, the latter a blue colour which inclines towards indigo. In fact, the absorption of the free hydroxyazo-compound and its alkali salts are entirely different in type, and the assumption that the remarkable colour change is accompanied by change of structure appears to have a certain justification. We drew specific attention to this point (*loc. cit.*, pp. 18, 19) and pointed out that Bamberger's brownish-red *p*-nitrobenzeneazo-α-naphthol (*Ber.*, 1895, **28**, 848; compare Hantzsch, *ibid.*, 1124) gave violet alkaline solutions. Taking into account the considerable probability of the salts of nitrophenols being derived from nitronic acids,

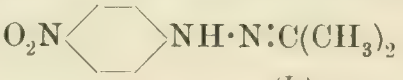


a hypothesis which has recently received very great support from Hantzsch's discovery of the *aci*-nitrophenol ethers (*Ber.*, 1906, **39**, 1084, 3072), we suggested that the relationship of *p*-nitrobenzeneazo-α-naphthol to its potassium salt was to be represented by the following formulæ:

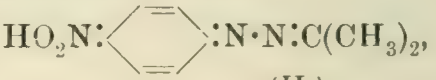


since no other alternative seemed possible.

Shortly after the appearance of our paper Baly and Tuck (Trans., 1906, **89**, 982) examined the absorption spectra of a number of phenylhydrazones of aldehydes and ketones, and the colour of the *p*-nitrophenylhydrazones as well as their solubility in alkali led these authors to assign to them a quinonoid constitution. Thus of the two possible formulæ for acetone-*p*-nitrophenylhydrazone,

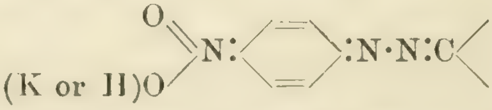


(I.)



(II.)

Baly and Tuck prefer the latter. The grouping



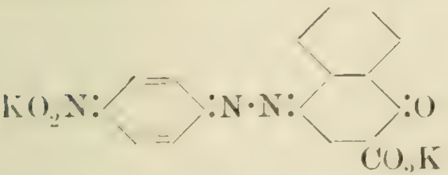
is common both to Baly and Tuck's formula for *p*-nitrophenylhydrazones and the structure we had already assigned to the alkaline salts of 4-nitro-4′-hydroxyazo-compounds.

If the above assumptions are correct, it would appear that the transformation of the nitroazo-structure to the *iso*nitro-*iso*azo-form is always accompanied by such a reduction in the oscillation frequency of the molecule that absorption bands are produced in the yellow or red end of the spectrum with the result that solutions appear red, violet, or blue by transmitted light.

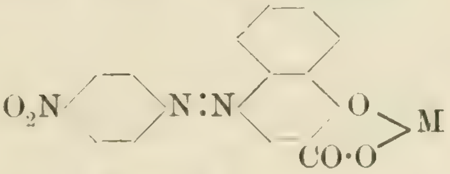
Whilst we adopt the standpoint advocated both by Baly and by Hantzsch, that a radical change in the absorption spectrum of a compound when it undergoes transformation into a salt means generally the radical alteration of its constitution, we have nevertheless considered it necessary to furnish definite proof of the constitution we advocated in our paper.

It is a well-known fact that the formation of lakes from hydroxyl-derivatives of aromatic compounds and salts of the heavy metals is conditioned by the aromatic compound containing two hydroxylic groups (generally both hydroxyl; for example, alizarin: sometimes one hydroxyl, one carboxyl; for example, azo-derivatives of salicylic acid) in the ortho-position relative to one another (C. Liebermann and St. von Kostanecki, *Ber.*, 1885, **18**, 2145, and subsequent authors). In view of the theory advocated in this paper one is not surprised to find that the brown *p*-nitrobenzene-4-azo-1-naphthol-2-carboxylic acid furnished violet-blue solutions in alkali, but even in presence of considerable excess of the latter gave brown precipitates with the salts of heavy metals. To prove the point it was necessary to show that the isomeric *p*-nitro-*m*-carboxybenzene-4-azo-α-naphthol not merely gave violet-blue or blue solutions in alkalis, but that precipitates of blue or violet shade might be obtained on adding the salts of heavy metals. The preparation of the necessary 2-nitro-5-aminobenzoic acid proved somewhat troublesome, but once in possession of the substance it was easily shown that by diazotisation and coupling with α-naphthol, a brown azo-acid was formed giving a blue solution in alkali and blue precipitates with the salts of heavy metals.

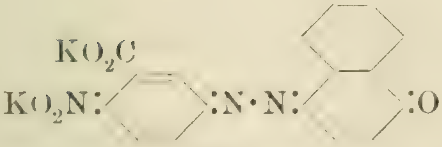
The constitution of the alkaline solutions and heavy metal precipitates of the two isomeric carboxylic acids derived from *p*-nitrobenzeneazo-α-naphthol can be represented in the following manner:



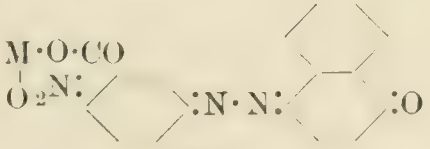
(blue)



(brown)

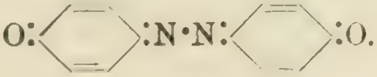


(blue)



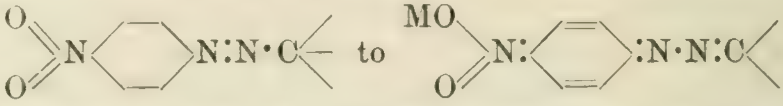
(blue)

It may be pointed out that the blue salts described in this paper are nearly related in structure to *p*-benzoquinoneazine:



This substance has been recently isolated by Willstätter and Benz (*Ber.*, 1906, **39**, 3482), and these authors draw attention to the fact (*loc. cit.*, p. 3484) that the quinoneazine exhibits a far deeper orange-red colour in solution than the *p*-azophenol from which it is produced by oxidation with silver oxide or lead peroxide. It seems to have struck them more particularly in that Scholl's rule "Wenn Chromogene, die mehr als einen Chromophor enthalten, in der Weise reducirt werden, dass ein Theil der Chromophore erhalten bleibt, während der andere in auxochrome Gruppen verwandelt wird, so kann damit eine Vertiefung der Farbe verbunden sein" (*Ber.*, 1903, **36**, 3410, 3426) is not obeyed.

But as we have shown, the real factor in this class of compounds is that transformation from the grouping



is accompanied by a shifting of the absorption in the direction of light of greater wave-length.

Several isolated facts observed by different experimenters may be correlated. Meldola and Streatfeild (Trans., 1886, **49**, 627) describe *p*-*p*-dinitrodiazoaminobenzene as forming small yellow needles, soluble in alkalis (alcoholic or boiling aqueous solutions) with a splendid magenta-red colour; the ethyl ether, which from its fission products undoubtedly possesses the structure

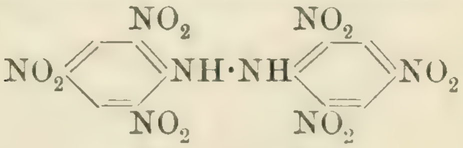
$$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2,$$

is, however, a yellow substance (*loc. cit.*, p. 630). We would suggest for the alkaline salts structures such as

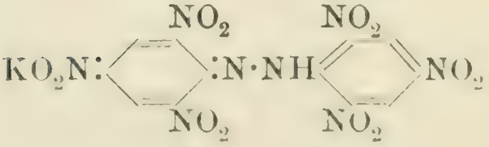
$$KO_2N{:}C_6H_4{:}N{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2,$$

resembling those we have ascribed to the *iso*nitro-*iso*azo-compounds.

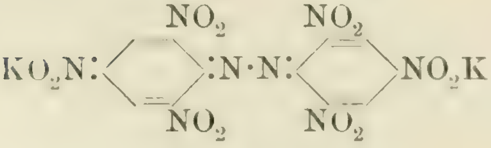
Grandmougin and Leeman (*Ber.*, 1906, **39**, 4384) have recently described the hexanitro-derivative of hydrazobenzene. This gives both mono- and di-potassium salts; the latter furnishes blue solutions. Evidently there is the same structural change in this case.



bright yellow.

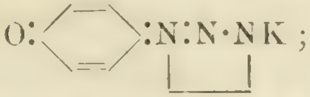


deep red solution in acetone.

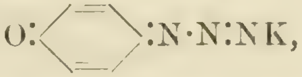


blue solution.

Finally the *p*-hydroxyphenylazoimide described by Forster and Fierz (Trans., 1907, **91**, 855) may possibly owe its remarkable change of colour in alkaline solution to a similar shifting of linkings. In the discussion following on the reading of this paper, Dr. Morgan suggested for the blue potassium salt the structure (Proc., 1907, **23**, 112):



and we venture to put forward the following formula,



as possibly representing the constitution of the substance; it is very similar to Dr. Morgan's, but obviates the quinquevalent nitrogen.

It is possible that a reaction discovered by Meldola may be explained by the alteration of structure suggested. Alkaline as well as acid-reducing agents generally decompose hydroxyazo-compounds at the double linking between the two nitrogen atoms, but when *p*-nitrobenzeneazophenol is warmed with ammonium sulphide in alkaline solution the nitro- is reduced to an amino-group (Trans., 1885, **47**, 659). This reaction may be compared with the reduction of nitrophenol to aminophenol under similar conditions.

It now becomes a matter of considerable interest to examine the behaviour of a number of nitrated azophenols and naphthols, in order to see if this diminution of oscillation-frequency generally accompanies the change from the hydroxyazo to the quinoneazine type, and, even if it is not possible to give a mechanical explanation, at least to discover the characteristic alteration in the molecule responsible for the change in the rate of oscillation.

Examination of several compounds has conclusively shown that *p*-nitroazophenols and the salts derived from them exhibit absorptions of radically different type, except in those cases where a group has been introduced which, in virtue of its character and position, can inhibit the production of diquinonoid structure. Other groups (for example, bromine atoms) when introduced in place of hydrogen may diminish the oscillation-frequency, but the effect in such cases is slight and the general character of the absorption remains unaltered.

It is, of course, conceivable that such groups, introduced into the molecule of a substance colourless in the ordinary sense, might, if its absorption occurs just outside the visible part of the spectrum, render the substance coloured by a slight shifting of the absorption-band. We are, however, in complete agreement with Baly and Hantzsch (*loc. cit.*), that when a radical change in colour (namely, absorption) takes place on salt-formation, the salt is constituted differently from the parent substance.

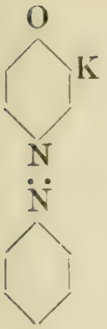
This is rendered very clear by comparing the absorptions of :

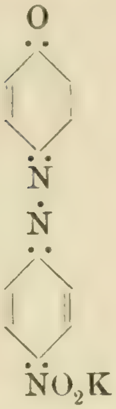
4-hydroxyazobenzene,
4'-nitro-4-hydroxyazobenzene,
3 : 5-dibromo-4'-nitro-4-hydroxyazobenzene,
and 3 : 4'-dinitro-4-hydroxyazobenzene.

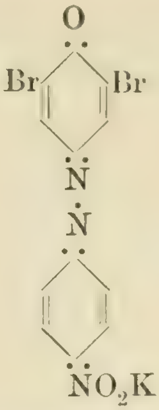
All four substances give alcoholic solutions of very similar yellow shade ; in *N*/500 solution the violet and blue are absorbed as far as wave-lengths 485, 506 and 510$\mu\mu$ respectively by the first three substances, whilst the fourth in *N*/1000 solution (too sparingly soluble in alcohol to admit of *N*/500) absorbs as far as 510$\mu\mu$. These four substances are essentially similarly constituted and their absorptions do not markedly differ, although it must be admitted that the nitro-group has a far more powerful effect than two bromine atoms.

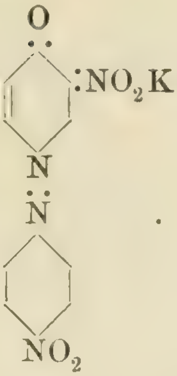
When, however, we compare the same solutions which have merely been treated with potassium hydroxide, very decided differences are apparent. The solution of 4-hydroxyazobenzene remains yellow but is much deeper in shade, the absorption extending as far as 495$\mu\mu$ in *N*/5000 solution : it will be observed that the alteration is one of degree rather than of character. An alkaline solution of 4'-nitro-4-hydroxyazobenzene is red (at *N*/20,000 the shade reminds one of cobalt nitrate solution) and the character of its absorption is entirely different from that of the free azophenol, a band appearing at this dilution between the limits 532—485$\mu\mu$. In the case of alkaline 3 : 5-dibromo-4'-nitro-4-hydroxyazobenzene the character of the absorption is found to be scarcely different from that of the unbrominated substance ; the band has slightly broadened and the maximum absorption has been shifted towards the red. Finally, if we take 3 : 4'-dinitro-4-hydroxyazobenzene, we find that conversion into an alkali salt intensifies the colour, but none of the blue or violet is transmitted, and on dilution no band makes its appearance, the absorption extending continuously from the ultraviolet into the visible spectrum.

The obvious explanation is that the second nitro-group being in the ortho-position relative to the hydroxyl, salt-formation preferentially takes place with production of ortho-quinonoid, and necessarily inhibition of paradiquinonoid structure. The potassium salts of these four azophenols may be represented structurally by the following formulæ :

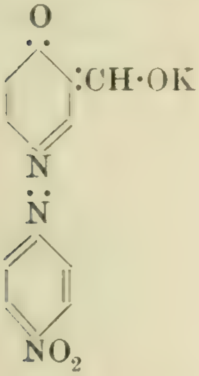


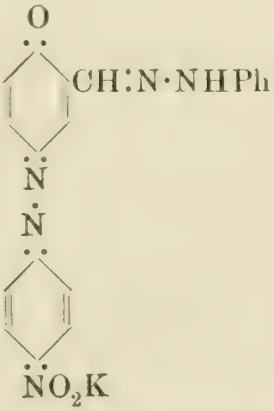


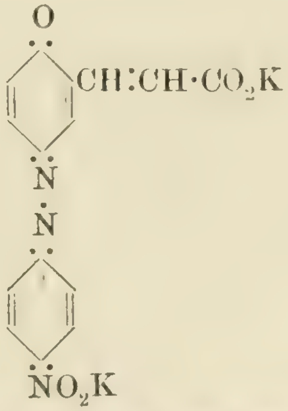




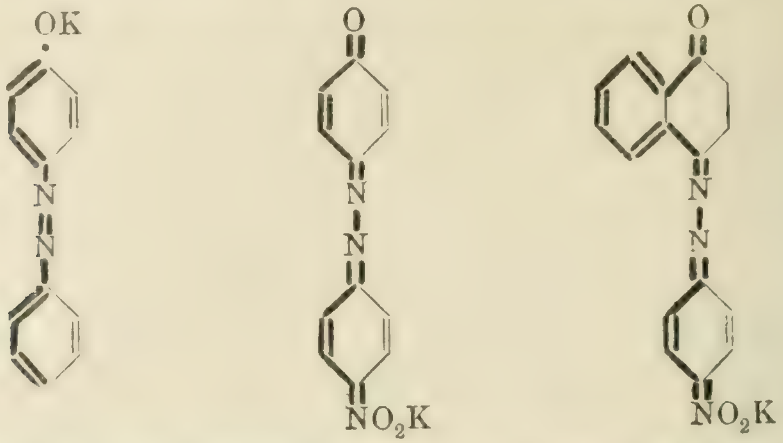
That this inhibiting action is not entirely restricted to an ortho-nitro-group is shown by the fact that *p*-nitrobenzeneazosalicylaldehyde, both in alcoholic and alkaline solutions, exhibits absorptions which are of the ordinary azo-type. Evidently salt-formation takes place with transformation of the grouping ·C(OH):C(CHO)· to ·C(:O)·C(:CH·OH)·. (Compare Hantzsch on the structure of salts of salicylaldehyde, *Ber.*, 1906, **39**, 3081, 3090.) But if the effect of the aldehyde group be nullified by conversion into a phenylhydrazone the substance dissolves in alcoholic potash with a magnificent purple colour, a band obliterating the green and part of the blue. The position of this band is almost identical with that exhibited by an alkaline solution of *p*-nitrobenzeneazocoumarin (Mitchell, Trans., 1905, **87**, 1231). The results are, in fact, quite to be expected when one compares the structure of the three alkaline salts:







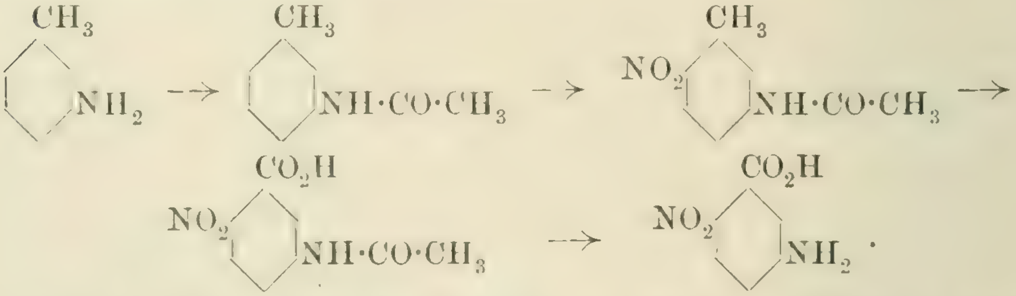
Amongst the compounds we have examined, the chief oscillation-frequency is less, the longer the chain of alternate double and single linkings existing in the molecule. In estimating the number of such alternate double and single linkings, when a benzene nucleus is encountered, one is only justified in following the structure round one side of the ring until the para-position is reached. If carried beyond the para-position the action becomes retrogressive and consequently no part of the particular displacement under consideration, but part of the succeeding, or return, displacement. If we compare the formulæ of the potassium salts of hydroxyazobenzene, *p*-nitrobenzeneazophenol, and *p*-nitrobenzeneazo-α-naphthol-β-carboxylic acid,



we see that the chain consists in the three cases of 5 double and 4 single, 6 double and 5 single, and 8 double and 7 single linkings respectively. On referring to our results it will be observed that they are in direct agreement with the view that the longer the chain the slower is the rate of oscillation.

EXPERIMENTAL.

2-*Nitro* 5-*aminobenzoic Acid.*—The only reference to this compound that we have been able to find deals with its preparation from α-dinitro-3-uraminobenzoic acid by boiling with water (Griess, *Ber.*, 1872, **5**, 198). Several alternative schemes for the production of this substance were devised and tried, the least unsatisfactory method proving to be the one outlined in the following way:



The aceto-*m*-toluidide was nitrated by adding it to fuming nitric acid. A mixture of nitro-products resulted, but it was found that the yield of the desired nitro-derivative was better when the reaction was allowed to proceed fairly rapidly, so that the temperature reached 15—20°. After pouring on to powdered ice, filtering and washing, the crude product was crystallised from benzene to which a little pyridine had been added.

The oxidation of the nitroacetotoluidide to the corresponding 2-nitro-5-acetylaminobenzoic acid was performed in the following manner.

Fifty grams of the finely-powdered substance were suspended in about 1 litre of water, steam was led in, and 75 grams of finely-powdered potassium permanganate were slowly added to the boiling liquid. After one and a half to two hours, the colour of the permanganate having been discharged, the precipitate of manganese dioxide was filtered off, and the filtrate, which immediately began to deposit crystalline matter, acidified with dilute hydrochloric acid, warmed in order to effect complete solution, and allowed to cool overnight. Part of the acetylamino-acid separated and a further amount was isolated by concentrating the mother liquor: in no case has a very satisfactory yield been obtained.

The free 2-nitro-5-aminobenzoic acid is obtained by hydrolysing the acetyl-derivative; in boiling with hydrochloric acid it is necessary to guard against too great a concentration of the latter; otherwise decomposition with gas evolution takes place, the carboxyl group being probably eliminated. The free acid gives a beautiful golden-yellow solution in boiling water, in which it is readily soluble and from which it is best recrystallised. When prepared in this way, 2-nitro-5-aminobenzoic acid forms fine golden-yellow needles, readily soluble in most organic liquids and melting at about 235° with considerable decomposition: *

0·1050 gave 0·1770 CO_2 and 0·0307 H_2O. C = 46·0; H = 3·3.

$C_7H_6O_4N_2$ requires C = 46·1; H = 3·3 per cent.

An aqueous solution of the ammonium salt of this acid gave the following reactions with the solutions of metallic salts:

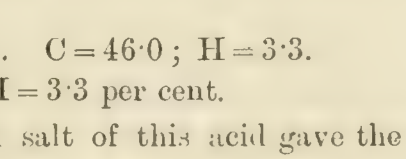
Silver nitrate.—Yellow precipitate, rapidly darkening on exposure. *Copper sulphate.*—Deep green solution, no precipitate. *Barium chloride.*—No precipitate. *Zinc sulphate.*—Slightly flocculent precipitate. *Mercuric chloride.*—Yellow precipitate.

2-*Nitro-5-acetylaminobenzoic acid* separates from boiling water in pale brown crystals which are readily soluble in organic solvents and melt at about 210—220° with decomposition.

0·1409 gave 0·2493 CO_2 and 0·0474 H_2O. C = 48·3; H = 3·7.

$C_9H_8O_5N_2$ requires C = 48·2; H = 3·6 per cent.

p-*Nitro*-m-*carboxybenzene-4-azo-α-naphthol*,



was prepared by diazotising the nitroamino-acid previously mentioned and coupling with a solution of α-naphthol in aqueous sodium hydroxide. The resulting blue, alkaline solution was acidified and the precipitated compound washed, dried, and crystallised from pyridine. It was subsequently recrystallised from the same solvent and warmed with dilute hydrochloric acid to remove all traces of pyridine. As thus obtained it formed a chocolate-coloured crystalline powder, which under the microscope proved to consist of aggregates of well-defined reddish-brown prisms. The substance melts near 260° with decomposition, and is sparingly soluble in most organic liquids forming yellowish-brown solutions. The alkaline solution exhibits an intense indigo-blue colour, and a similar colour is observed in concentrated sulphuric acid solution:

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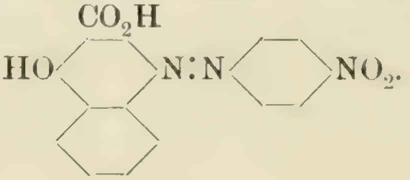
* As, almost without exception, the substances described in this paper melt with considerable decomposition at elevated temperatures, the melting points have not been corrected for the relative coefficient of expansion of mercury.

0·1671 gave 18·2 c.c. moist nitrogen at 21° and 756 mm. N = 12·6.
$C_{17}H_{11}O_5N_3$ requires N = 12·5 per cent.

On adding lead acetate to the alkaline solution a blue precipitate is obtained.

p-*Nitrobenzene*-4-*azo*-1-*naphthol*-2-*carboxylic acid*,



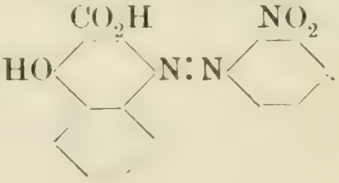
This compound, to which the authors have already drawn attention (Trans., 1906, **89**, 19), results from the coupling of *p*-nitrodiazobenzene salts with 1-naphthol-2-carboxylic acid. In appearance it closely resembles the isomeride just described; it melts fairly sharply about 242°, but immediately decomposes. It is soluble in nitrobenzene, pyridine, or chloroform, more sparingly so in alcohol or other organic solvents; for crystallisation nitrobenzene proved most convenient. The solution in alkalis is deep blue, but on addition of lead acetate to the alkaline solution a reddish-brown precipitate is produced. Analysis of the free acid gave the following result:

0·1146 gave 12·6 c.c. moist nitrogen at 19° and 756 mm. N = 12·8.
$C_{17}H_{11}O_5N_3$ requires N = 12·5 per cent.

This compound dissolves in sulphuric acid with an indigo-blue coloration.

For purposes of comparison the ortho- and meta-nitro-derivatives were prepared and examined.

o-*Nitrobenzene*-4-*azo*-1-*naphthol*-2-*carboxylic acid*,

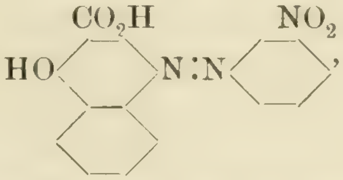


was prepared in a similar manner from diazotised *o*-nitroaniline. By crystallisation from chloroform aggregates of small brown prisms were obtained which melt with decomposition at 200°:

0·0531 gave 0·1173 CO_2 and 0·0186 H_2O. C = 60·3 ; H = 3·8.
$C_{17}H_{11}O_5N_3$ requires C = 60·5 ; H = 3·3 per cent.

The substance is sparingly soluble in alcohol or the usual organic solvents giving reddish-brown solutions. Alkalis dissolve it with production of a permanganate shade, whilst in strong sulphuric acid an indigo-blue solution is obtained.

m-*Nitrobenzene*-4-*azo*-1-*naphthol*-2-*carboxylic acid*,

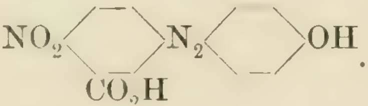


from diazotised *m*-nitroaniline and naphtholcarboxylic acid, separated from glacial acetic acid in small brown crystals. It melts with decomposition at 220—225° and in its behaviour towards organic solvents much resembles its isomerides. In alkali the colour is, however, reddish-purple, whilst in strong sulphuric acid it is bluish-purple:

0·1000 gave 10·2 c.c. moist nitrogen at 15° and 763 mm. N = 12·2.
$C_{17}H_{11}O_5N_3$ requires N = 12·5 per cent.

The nature of the absorption in the visible part of the spectrum of some of the compounds described in this paper, together with that of several other nitrated azophenols, will be found in a table at the end.

p-*Nitro*-m-*carboxybenzeneazophenol*,



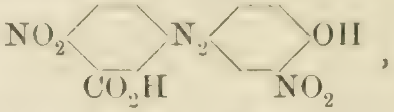
2-Nitro-5-aminobenzoic acid was diazotised and coupled with phenol. The resulting alkaline solution was intensely blood-red.

The azophenol was precipitated by acidification and crystallised twice from boiling dilute acetic acid, when it formed deep red needles which melted at 195°.

This azophenol is readily soluble in the usual organic solvents, and is sparingly soluble in boiling water.

Unfortunately, we are unable to give direct analytical data with respect to this particular substance, as the combustion was accidentally spoiled, and we had not a sufficient quantity left for analysis. Its mode of preparation and properties, however, leave no doubt as to its nature, and the derivative about to be described gave very satisfactory analytical figures.

p-*Nitro* m-*carboxybenzeneazo*-o-*nitrophenol*,



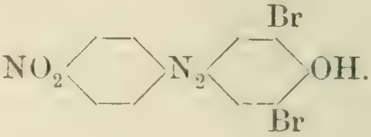
was prepared by dissolving the above-described compound in concentrated sulphuric acid and adding the calculated quantity of nitric acid of sp. gr. 1·42.

After standing three hours the mixture was poured into a large excess of water and the precipitated dinitro-compound collected, washed, and dried.

After crystallisation from boiling dilute acetic acid it formed small, well-defined reddish-yellow needles, readily soluble in glacial acetic acid, alcohol, chloroform, etc., and melting at 214°:

0·1960 gave 0·0446 H_2O and 0·3359 CO_2. C = 46·7; H = 2·5.
$C_{13}H_8O_7N_4$ requires C = 46·9; H = 2·4 per cent.

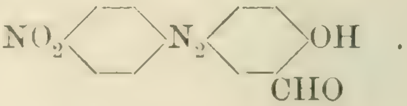
p-*Nitrobenzeneazo*-o-o-*dibromophenol*,



Finely-powdered *p*-nitrobenzeneazophenol was stirred into glacial acetic acid, an excess of powdered fused sodium acetate being added, and finally the calculated quantity of bromine, the latter diluted with glacial acetic acid. The mass gradually thickened, changing in appearance from red to brown. After half an hour it was diluted largely, filtered, and the dibromo-derivative crystallised twice from glacial acetic acid. It formed lustrous, brownish-golden flattened prisms, melting at 205—206°. This substance is soluble in alkali with an intense red colour, and also dissolves in alcohol, acetone, benzene, or chloroform, but is insoluble in light petroleum:

0·3234 gave 0·4326 CO_2 and 0·0545 H_2O. C = 36·4; H = 1·9.
$C_{12}H_7O_3N_3Br_2$ requires C = 35·9; H = 1·7 per cent.

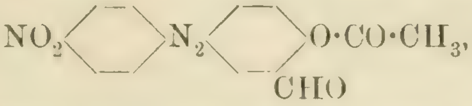
p-*Nitrobenzeneazosalicylaldehyde*,



A diazotised solution of *p*-nitroaniline was added to the calculated quantity of salicylaldehyde dissolved in water containing excess of sodium carbonate and a little sodium hydroxide. After two hours the liquid was acidified, the azo-compound collected, washed, dried, and crystallised twice from toluene. From this solvent it separated in small, flattened, red needles, melting at 192—193°. This substance is soluble in alcohol, ether, acetone, or glacial acetic acid, giving reddish-yellow solutions, and in alkali it is also yellow.

Concentrated sulphuric acid dissolves it with the production of a yellowish-brown colour:

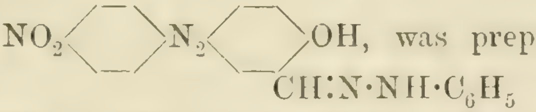
0·2761 gave 0·1004 H_2O and 0·5791 CO_2. C = 57·2; H = 4·0.
$C_{15}H_{11}O_5N_3$ requires C = 57·5; H = 3·5 per cent.

The *acetyl* derivative, 

, was prepared by boiling the parent substance (1 gram) with its own weight of fused sodium acetate and four times its weight of acetic anhydride for about two hours. It separated from glacial acetic acid in small, yellow nodules, which did not exhibit any very definite crystalline form.

This substance is sparingly soluble in alcohol or benzene, but is readily dissolved by chloroform or acetone, yielding yellowish-red solutions. It is insoluble in light petroleum and melts at 150°:

0·2103 gave 0·0731 H_2O and 0·4415 CO_2. C = 57·4; H = 3·8.
$C_{13}H_9O_4N_3$ requires C = 57·5; H = 3·3 per cent.

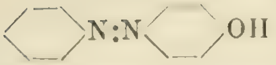
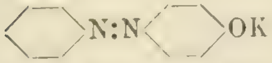
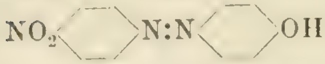
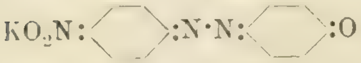
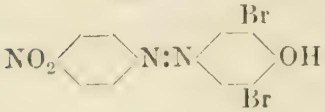
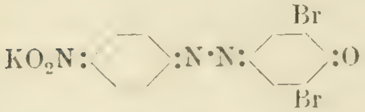
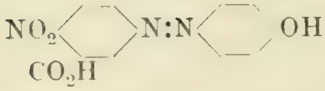
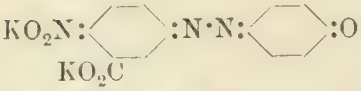
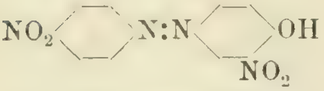
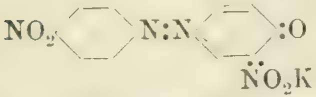
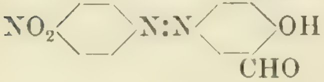
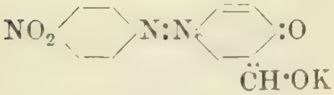
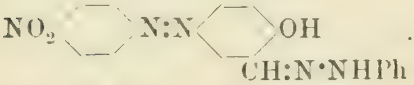
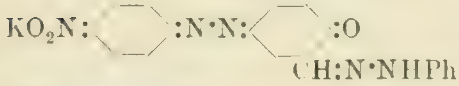
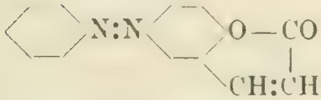
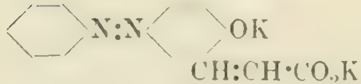
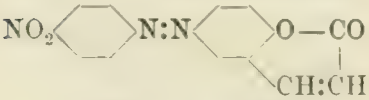
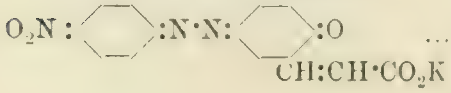
The *phenylhydrazone*, 

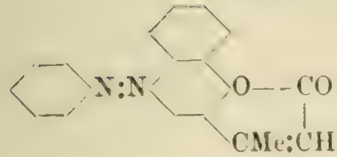
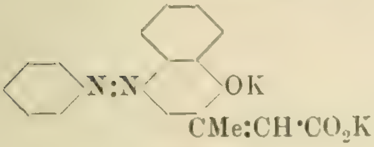
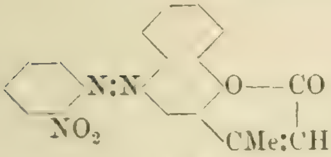
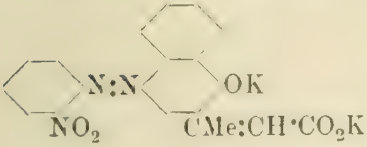
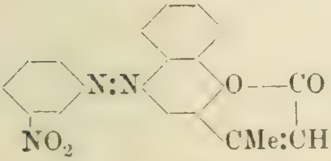
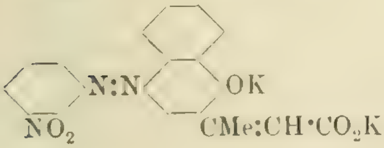
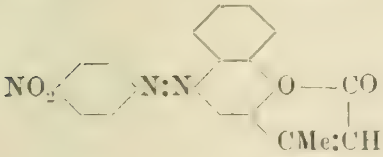
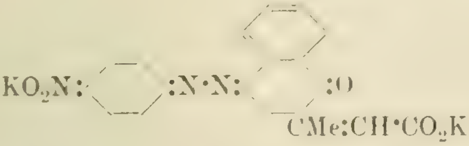
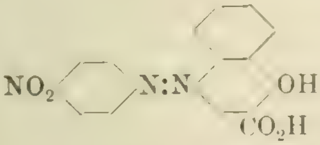
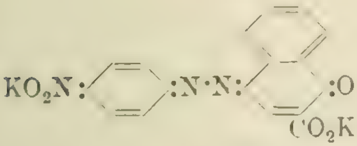
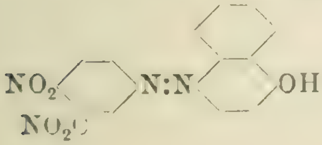
, was prepared by stirring the finely-powdered azoaldehyde in glacial acetic acid containing excess of fused sodium acetate and adding a solution of phenylhydrazine acetate in glacial acetic acid. The resulting mixture rapidly thickened, the hydrazone was collected, washed with a little glacial acetic acid, and crystallised from the same substance. It formed shining, deep red laminæ, which melted at 235—240° with much decomposition.

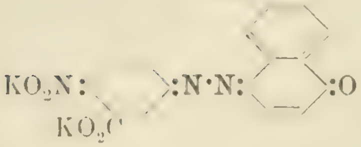
This substance dissolves sparingly in alcohol, acetone, chloroform, or benzene with a yellow colour, whilst in alcoholic potash the colour is a beautiful bluish-purple:

0·1873 gave 0·0754 H_2O and 0·4339 CO_2. C = 63·2; H = 4·5.
$C_{19}H_{15}O_3N_5$ requires C = 63·2; H = 4·2 per cent.

In recording the observations made with the aid of the spectroscope, it must be noted that only the visible part of the spectrum has been examined. In the following table such a statement as "To wavelength 610 $\mu\mu$" indicates that the red end of the spectrum is absorbed as far as 610 $\mu\mu$, whilst "From 524 $\mu\mu$ onwards" means that from 524 $\mu\mu$ onwards the blue and violet are absorbed as far as the visible spectrum extends. All the solutions examined were alcoholic, solutions of the potassium salts being prepared by adding a drop of 50 per cent. potassium hydroxide solution to the alcoholic solution of the parent phenol.

Substance.	Concentration.	Absorption (Red) (Violet).
	N/500	From 485 $\mu\mu$ onwards.
	N/5000	From 495 $\mu\mu$ onwards.
	N/500	From 506 $\mu\mu$ onwards.
	N/20,000	Band 532—485 $\mu\mu$.
	N/500	From 510 $\mu\mu$ onwards.
	N/20,000	Band 550—480 $\mu\mu$.
	N/1000	From 457 $\mu\mu$ onwards.
	N/10,000	Band 540—460 $\mu\mu$.
	N/1000	From 510 $\mu\mu$ onwards.
	N/1000	From 562 $\mu\mu$ onwards.
	N/500	From 550 $\mu\mu$ onwards.
	N/2000	From 550 $\mu\mu$ onwards.
	N/500	From 517 $\mu\mu$ onwards.
	N/10,000	Band 550 to 475 $\mu\mu$.
	N/500	From 480 $\mu\mu$ onwards.
	N/500	From 520 $\mu\mu$ onwards.
	N/500	From 498 $\mu\mu$ onwards.
	N/10,000	Band 550 to 465 $\mu\mu$.

Substance.	Concentration.	Absorption (Red) (Violet).
	*N*/500	From 541 $\mu\mu$ onwards.
	*N*/2000	From 561 $\mu\mu$ onwards.
	*N*/500	From 541 $\mu\mu$ onwards.
	*N*/5000	Band 583 to 510 $\mu\mu$.
	*N*/500	From 524 $\mu\mu$ onwards.
	*N*/5000	Band 590 to 480 $\mu\mu$.
	*N*/1000	From 500 $\mu\mu$ onwards.
	*N*/2000	*To* wave-length 580 $\mu\mu$.
	*N*/500	From 572 $\mu\mu$ onwards.
	*N*/10,000	*To* wave-length 610 $\mu\mu$.
	*N*/500	From 540 $\mu\mu$ onwards.

Substance.	Concentration.	Absorption (Red)	(Violet).
	N/10,000	*To* 550 $\mu\mu$.	

EAST LONDON COLLEGE.

CXVIII.—*Some Properties of Radium Emanation.*

By ALEXANDER THOMAS CAMERON, M.A., B.Sc., and SIR WILLIAM RAMSAY, K.C.B., F.R.S.

IN a recent communication to this Society by one of the authors, the properties of the emanation from radium, so far as they were known, have been succinctly described. The present research has reference to the volume of that gas obtained from a known amount of radium bromide in a given time; to its behaviour as regards pressure and temperature; and to the changes in volume which it undergoes spontaneously.

Two experiments are on record, by Mr. Soddy and one of the authors (*Proc. Roy. Soc.*, 1904, **73**, 346), in which contradictory results were obtained. The emanation in the first experiment underwent rapid contraction in the first few hours and then contracted at a slower rate, corresponding to the decay as shown by electrical measurement. In the second experiment there was a continuous increase of volume, due, apparently, to the spontaneous change of the emanation into a larger volume of helium. The cause of this change was attributed to the different quality of the glass of the capillary tubing used in each case.

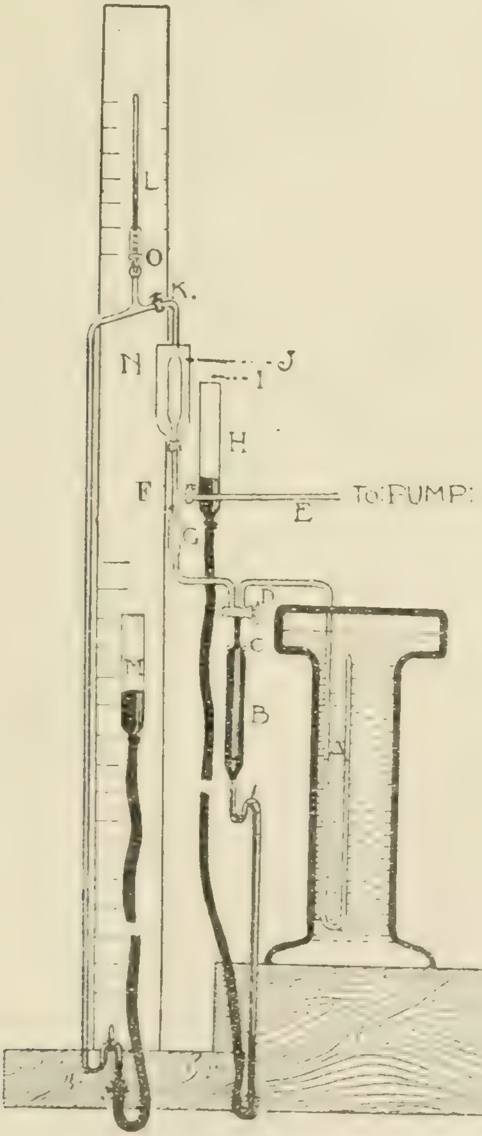
We have now found that in all cases the emanation undergoes a rapid change of volume in a short period of time, and that this change is followed by a slow change, corresponding with its loss of electrical activity. In order to gain knowledge of the effect of adhesion of gases to the walls of tubes such as those used, we have studied the behaviour of helium and of carbon dioxide in contact with glass and with silica; and we have carried out experiments which prove that the emanation, although abnormal in its behaviour to temperature, follows Boyle's law closely. We have also made several measurements of the volume of emanation obtainable from a known weight of radium in a given time.

(1) *Apparatus Employed, and Method of Experiment.*—The

apparatus, although resembling that employed in the research alluded to (Ramsay and Soddy, *loc. cit.*), was so much modified as to demand a detailed description.

The gases extracted from 151 milligrams of radium bromide (supposed to contain $2H_2O$ of crystallisation) and 10 milligrams of sulphate, or in all, taking the atomic weight of radium as 225, 87·7 milligrams of metallic radium, consisted of a mixture of hydrogen and oxygen, with a small excess of hydrogen. These gases were introduced through the inverted siphon A (Fig. 1) into the explosion-burette B, and a spark was passed between the electrodes at C, the stopcock D being shut. The apparatus was pumped completely empty of air through E, and the stopcock F was closed. The tap D was then opened, and the small residue of hydrogen,

FIG. 1.



containing emanation, was allowed to escape up through the tube G, filled with phosphoric oxide, in order to keep back the water-vapour produced by the explosion. On raising the reservoir H the mercury was forced through the phosphoric oxide to a level a little below that of the tube leading to the pump. Liquid air was then poured into the jacket I, and J was cooled to −185°. The emanation condensed in J, and the hydrogen was pumped off through F until the bubbles became exceedingly minute and failed to pass down the capillary of the pump. The tap F was then shut and the level of the mercury in G raised until it was above that of the side-tube E. The liquid air was then allowed to evaporate, and when J had warmed to atmospheric temperature mercury was passed up until the emanation had entered the capillary tube L through the tap K; K was then closed. As mercury did not pass easily through the phosphoric oxide in G, it was found convenient to read pressure by means of a separate reservoir M, which could be raised or lowered opposite the mirror scale N. The scale was divided into millimetres and read to tenth-millimetres. A series of readings was taken immediately after the introduction of the emanation into the capillary L. In experiments 1 to 4 the capillary consisted of potash-lime glass, which had been cleaned with potassium dichromate and sulphuric acid and heated before being mounted. Two tubes specially selected for their regularity were used, and they are represented in the figure by dotted lines. For experiments 5 and 6 a silica capillary of exceptionally regular bore was employed; this was sealed to a larger silica tube, which was ground as a stopper into the glass enlargement at O. Special rubber-vaseline grease was used.

After one or two days the glass became dark brown, owing to the action of the emanation. This would have made reading difficult; but by always leaving the emanation under such high pressure that it occupied only a few millimetres at the top of the tube, the darkening was confined to that region. The silica tube, procured from Messrs. Baird and Tatlock, became dark blue; a silica tube from Heraeus remained perfectly colourless.

(2) *The Relation of Volume to Pressure.*—It had already been shown by Ramsay and Soddy that the values of P.V. for the emanation are practically constant. This has been confirmed by no fewer than thirty different sets of measurements. Three examples will be given; in the first the emanation had been in the tube 48 hours; the time occupied in making the measurements was about ten minutes. Helium had been formed, but was completely absorbed by the walls of the tube.

Temperature.	Pressure, mm.	Volume, cub. mm.	P.V.
10·8°	23·3	7·64	178·0
	29·7	5·98	177·7
	35·2	5·04	177·3
	45·4	3·95	179·3
	45·7	3·92	179·1
	58·9	3·07	180·7
	66·8	2·65	177·0
	76·9	2·31	177·7
	96·2	1·95	187·5
	118·1	1·44	170·6
	139·6	1·22	170·8

As an example of readings of the volume of the emanation immediately after it had been introduced into the capillary, the following numbers may be given:

Temperature.	Pressure, mm.	Volume, cub. mm.	P.V.
17·9°	28·0	10·08	282·2
	36·3	7·36	267·0
	53·5	5·04	269·5
	95·5	2·80	267·1
	235·1	1·11	260·0

These observations were made within five minutes after compression into the capillary tube; the next table shows the values an hour and a half after, when the first change was nearly complete:

Temperature.	Pressure, mm.	Volume, cub. mm.	P.V.
16·9°	195·7	0·70	137·5
	70·7	2·02	143·1
	42·2	3·54	149·3
	25·0	5·92	148·0
	18·2	8·39	152·7

As the top of the tube was an approximate cone, it was assumed to be a true cone, and allowance was made for its volume accordingly.

(3) *Measurement of Initial Volume.*—When the volume was observed immediately after transference to the capillary tube the results were the following:

	Time of accumulation, days.	Actual volume, cub. mm.	Volume per 3·86* days, cub. mm.
Ramsay and Soddy (1903) ...	8	0·339 (0·124)†	0·222
I. First glass tube	4	0·345	0·337
II. ,, ,, ...	8	0·299	0·196
III. Second ,, ...	5·12	0·333	0·277
V. Silica ,, ...	5	0·375	0·316
VI. ,, ,, ...	4	0·187	0·182

* Sackur's value for the half-period of the emanation, determined in the laboratory of University College, has been used; it is nearly the mean of Curie's and Rutherford's (*Ber.*, 1905, **38**, 1756).

† A different quantity of radium bromide was used; the figure in brackets represents the actual amount observed.

It will be noticed that the calculated volume for the period of half-decay of the emanation varied from 0·182 to 0·337 cub. mm. We consider this due to the difficulty of determining the point at which all the hydrogen has been pumped off. Although Rutherford states otherwise, we have repeatedly confirmed the observation of Ramsay and Collie (*Proc. Roy. Soc.*, 1904, **73**, 474), that the emanation possesses a feeble vapour-pressure even at the temperature of liquid air. Hence, if all admixed gas is removed, some emanation volatilises with it, and judgment has to be used in determining the point at which pumping should cease. The observed discrepancies are probably to be attributed to this circumstance.

The larger volumes observed in experiments I, III, and V probably approximate to the correct value; in the other cases the pumping was carried much further, and emanation was probably removed. It will be shown immediately that within an hour and a half after the first measurement of the emanation its volume spontaneously decreases to half; now this was observed in experiments V and VI, and affords a strong presumption that the tube contained pure emanation, for had foreign gas been present the half-rates would obviously not have been attained. The larger of the two volumes, 0·375 cub. mm. of emanation for five days' accumulation from radium bromide, is probably even still less than the correct amount which is produced in that time. The mean of the three experiments I, III, and V, for the period of half-decay, namely, 3·86 days, gives 0·310 cub. mm. as the volume of emanation produced; even this, however, must be taken as a minimum. The mean of all five experiments is 0·262 cub. mm.

(4) *Sudden Change of Initial Volume.*—Ramsay and Soddy observed in their first experiment a very marked diminution in volume within the first twenty-four hours; further observations have now been made of this very curious behaviour. It appeared that in little more than an hour the sudden contraction ceased. The following results were obtained:

	Initial volume, cub. mm.	Volume after rapid contraction.	Decrease, per cent.	Time, in hours.
(Ramsay and Soddy ...	0·124	0·027	—	24)
Expt. III	0·333	0·181	45·6	0·75
,, IV	0·058	0·0275	52·6	1·0
,, V	0·397 (single reading)	0·194	51·1	1·5
,, VI	0·187	0·085	54·5	1·25

In each case the volume has decreased just over 50 per cent. in an hour. In experiments III and IV only single observations were made; the detailed observations in V and VI are next given. Each volume was measured in these two sets by a single reading only; in experiment V the pressure varied from 503·9 to 517·0; in VI, from 483·5 to 488·2.

Experiment V.

Time, minutes.	Volume, cub. mm.
0	0·397
15	0·351
22	0·291
30	0·247
45	0·205
61	0·199
95	0·194

Experiment VI.

Time, minutes.	Volume, cub. mm.
0	0·187
7	0·147
11	0·129
14	0·118
16·5	0·110
20	0·104
25	0·101
36	0·092
45	0·090
64	0·087
75	0·085

The numbers of experiment V are graphically represented in curve I (Fig. 2), and those of experiment VI in curve II (Fig. 2). The break in curve I is to be attributed to the fact that between the first and second readings a series of measurements at varying pressures was made.

These curves are exponential. Taking the figures of experiment VI and subtracting from each the final figure 0·085, the figures given in the second column below are obtained. The figures given in the third column are calculated by means of the equation

$$V_{o}/V_t = e^{-\Lambda t},$$

where V_0, the initial volume, is taken as 0·102, V_t is the volume at time t, and Λ is calculated from $t=0$, $V=0·102$; $t=11$, $V=0·044$; the value of Λ is 0·0764, giving a half-change period of 9·07 minutes. The figures in the fourth column are those of the constant k, derived from the equation

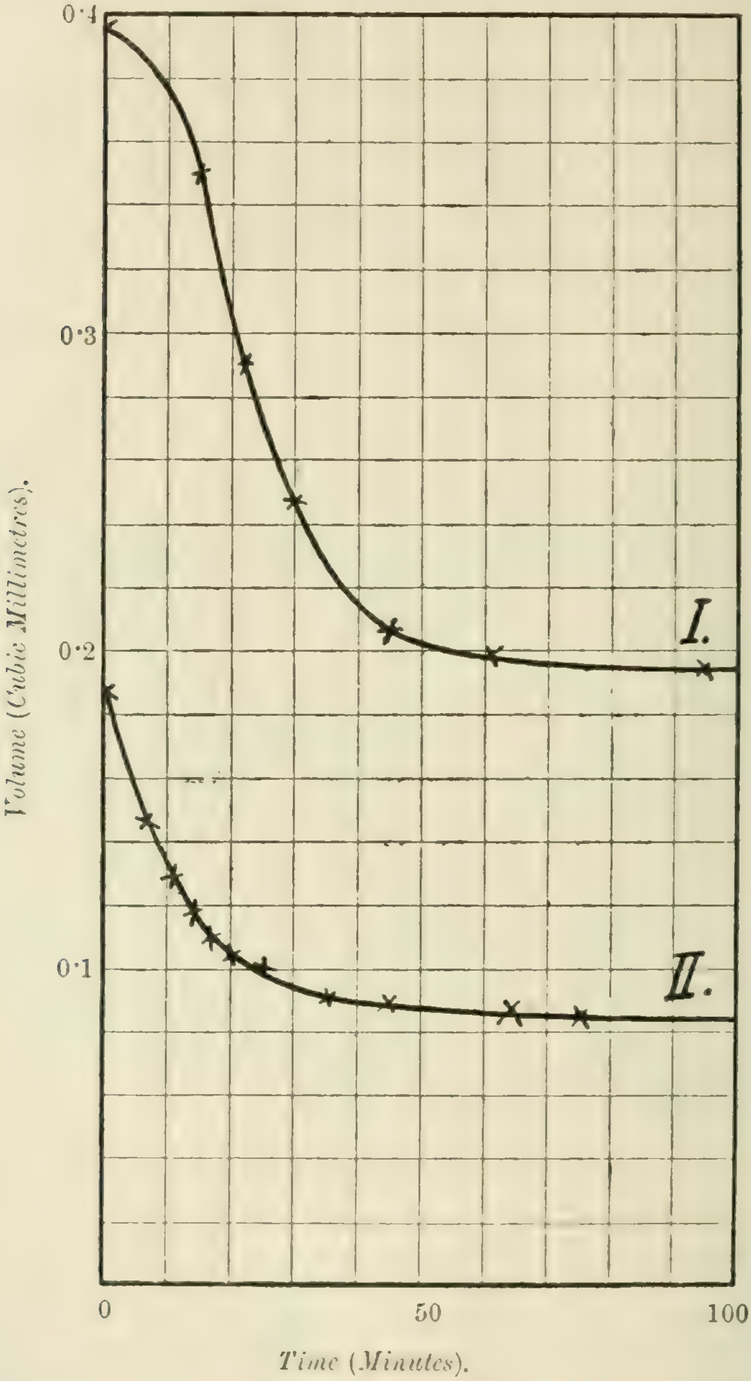
$$k = \Lambda \log e = 1/t \log \frac{V_t}{V_o}.$$

Time.	Volume.	Calculated volume.	k.
0	0·102	(0·102)	—
7	0·062	0·060	0·0319
11	0·044	(0·044)	0·0332
14	0·033	0·035	0·0350
16·5	0·025	0·029	0·0370
20	0·019	0·022	0·0365
25	0·016	0·015	0·0322
36	0·007	0·0065	0·0323
45	0·003	0·0033	0·0310
64	0·002	0·0008	0·0267
75	0·000	0·0003	0·0268

The logarithms of these volumes are shown, plotted against time, in Fig. 3.

The only possible hypotheses to account for this change are: (1) adsorption by the glass or silica or a phenomenon of similar nature; or (2) some hitherto unnoted change in the emanation itself. We shall show later that adsorption can only account for 2 or 3 per cent. of this change at a maximum; and it is remark-

FIG. 2.

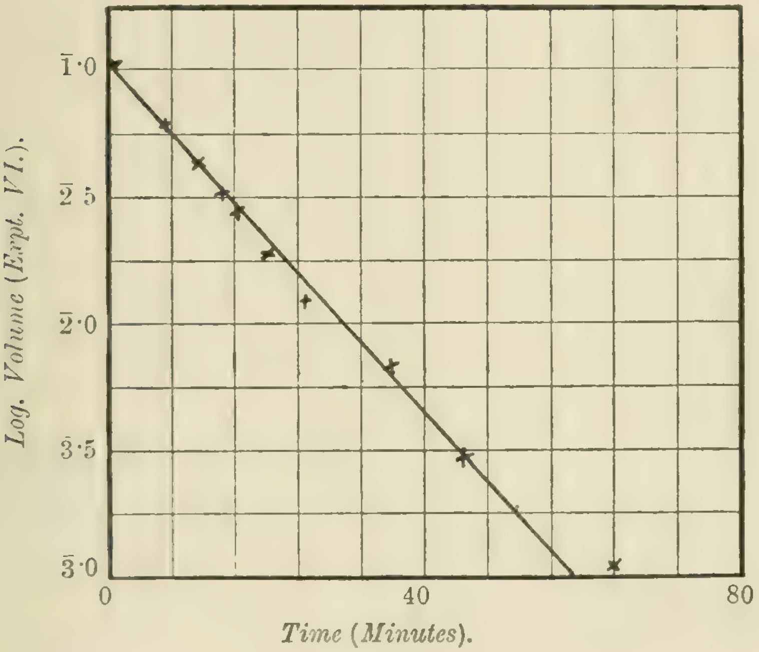


able that after correction for adsorption the contraction is, within the limits of error, 50 per cent. Within the extreme period of measurement, an hour and a half, the decay, according to electrical measurements, should be 1·13 per cent. The discussion of the actual cause of this change is reserved until later.

(5) *Details of Experiments.*—In all cases the volume is corrected to 0° and 760 mm. pressure.

Experiment I.—A glass tube A of 0·448 mm. diameter and having a correction for capillarity of 21·2 mm. was charged with the emanation collected in four days from 87·7 milligrams of radium present as bromide and sulphate. The volume was read at intervals.

FIG. 3.



Time, in days.	No. of observations.	Limits of P.V.	Volume, cub. mm.	Volume, calculated from known rate of decay determined electrically, cub. mm.
0·0	5	269·0—274·1	0·345	(0·345)
0·04	10	233·6—253·6	0·310	0·342
0·80	9	182·4—203·1	0·247	0·299
1·81	11	170·6—187·5	0·225	0·249
2·81	10	148·0—159·0	0·195	0·208
3·83	8	150·4—161·6	0·198	0·173

To this quantity 4·13 days' accumulation of emanation was added, and the total volume observed was then 0·840 cub. mm. After forty-eight hours this had altered to 2·044 cub. mm., the increase being largely due to leakage through the tap. There was no further leakage, but the volume increased steadily for eight days; the final (constant) volume was 2·436 cub. mm. The tube was then heated to expel helium, and the final volume was 2·841 cub. mm. On heating the tube the brown colour disappeared at a comparatively low temperature, and a deposit showing a submetallic lustre was noticed at the very top of the tube into which the gas was compressed after taking measurements, so as to avoid discolouring it. We regard this deposit as probably radium *D* (see below). It will be observed that the immediate decay was not noticed in this case; it was the first experiment, and it is probable that hydrogen was not thoroughly pumped away.

It is possible to deduce from these results an approximate ratio between the volumes of the emanation and the helium to which it gives rise. Assuming the volume of the emanation produced by the radium in 3·86 days to be 0·310 cub. mm., in four days 0·318 cub. mm. should be obtained. The total theoretical quantity in eight days will be 1·5 times this amount, = 0·477 cub. mm. From the curve of increase, the leak in the first two days can be measured; it is approximately 0·960 cub. mm. The total quantity of other gas present is therefore (0·840 − 0·477) + 0·960 = 1·323. Taking the final value 2·841 as correct, the amount of helium present is (2·841 − 1·323) = 1·518. The ratio of helium to emanation is thus 1·518/0·477 = 3·18.

Experiment II.—The same capillary A was employed. The initial volume obtained from eight days' accumulation was 0·299 cub. mm. Through leakage in the tap the volume increased in twenty-four hours to 3·112 cub. mm. A series of observations was made, in which the volume gradually fell off, but no importance can be attached to them.

Experiment III.—The apparatus was altered to the form shown in the figure; the slope of the tube carrying the tap K was changed, and much inconvenience was thereby saved. A new glass tube, B, of the same glass as A, was substituted for A. Its diameter was 0·453 mm., and the correction for capillarity was 19·8 mm. The emanation was introduced after having accumulated for 5·12 days.

Time, in days.	No. of observations.	Limits of P.V.	Volume, cub. mm.	Volume calculated from known rate of decay determined electrically.
0·0	5	260·0—282·2	0·333	(Half = 0·167)
0·03	5	137·5—152·7	0·181	—
0·77	10	119·8—133·3	0·159	0·145
1·03	5	105·2—115·9	0·138	0·139
1·78	4	98·4—102·1	0·124	0·121
3·78	5	68·7— 88·7	0·096	0·085
4·80	5	60·5— 67·0	0·080	0·071

Experiment IV.—The glass tube B was filled with four days' accumulation; but in course of transference to the capillary tube a considerable quantity of air was accidentally admitted. In pumping this air out the greater part of the emanation was also removed.

Time, in days.	No. of observations.	Limits of P.V.	Volume, cub. mm.	Volume calculated from known rate of decay determined electrically.
0·0	8	45·6—48·6	0·058	(Half = 0·029)
0·04	5	19·1—26·3	0·0275	—
0·89	1	14·1—14·9	0·0178	0·0247
2·89	4	12·7—15·5	0·0172	0·0173

Experiment V.—We were fortunate in obtaining an exceptionally fine tube of silica; it gave much better results than the glass tubes, for the "sticktion" was much less, so little as to be practically negligible. The diameter of the tube was 0·208 mm.; its correction for capillarity was 45·4 mm. Five days' accumulation of radium emanation was introduced. The detailed measurements during the first hour and a half have already been cited on pp. 1270 and 1271. The remaining measurements are:

Time, in days.	No. of observations.	Limits of P.V.	Volume, cub. mm.
0·0	4	291·5—319·0	0·375
0·11	1		0·192
0·875	1		0·192
1·93	1		0·188
2·93	1		0·185

The volume diminished to half in about an hour and a half, as previously shown, thereafter remaining stationary. After the last reading, the tube was heated and cooled for three-quarters of an hour. The volume was 0·298 cub. mm.; it was then heated for an hour and a quarter, the initial reading being taken after cooling for half an hour. The following results were obtained:

Time, minutes.	Volume, cub. mm.	Time, minutes.	Volume, cub. mm.
0	0·471	95	0·181
20	0·269	120	0·179
75	0·197		

The large volume obtained at first must have been due either to an insufficient period of cooling or to the tube having been previously treated with helium (see below), part of which may have been given up. After a further 120 hours the volume fell to 0·169 cub. mm., remaining constant at this figure. The curve showing the rate of decay is strictly comparable with curves I. and II. (Fig. 2).

Experiment VI.—Emanation collected during four days was introduced into the same silica tube. The figures for the initial change have already been given on pp. 1270 and 1271. The further change is shown below:

Time, in days.	Volume, cub. mm.	Calculated volume.
0·0	0·187	(Half = 0·093)
0·875	0·079	0·079
2·85	0·066	0·056
3·85	(0·079)	—

As soon as the first change was completed, the effect due to change of temperature was investigated by jacketing the tube with the vapour of benzene and of chlorobenzene boiling respectively at 80° and 132°. The change due to the higher temperature was observed during the second, third, and fourth days; finally an experiment was carried out with quinoline as a jacket (237°), but owing to the entrance of a trace of air at the junction of the silica with the glass, there was some uncertainty as to the true pressure.

In the annexed table the results under the heading "dissociation" were calculated on the assumption that the rapid change to half-volume is due to association, and that the change of temperature has resulted in partial dissociation. From the observed volume the theoretical volume at 0° and 760 mm. pressure is calculated and the quotient (volume at T° corrected to 0° and 760 mm.) divided by (volume at *t*° corrected to 0° and 760 mm.), T being the temperature of the hot vapour and *t* that of the room, represents the volume resulting from two volumes of the original, or from one volume of the associated, gas. The results are most remarkable, inasmuch as, were we to suppose that the increase is due to the liberation of helium from the walls of the tube (which, as will be described below, had been already treated with helium), the volume should be greater the higher the temperature; but the volume at 132° is less than that at 80° (both reduced to 0°); and this observation also puts out of court the possible suggestion that the initial change of volume is to be ascribed to adsorption. The results are seen in the accompanying table (the original volume of emanation was 0·187 cub. mm.):

Time.	Temperature.	Pressure, mm.	Volume observed, cub. mm., corrected to 760 mm.	Dissociation.
April 12th, 5.20 p.m....	80°	483·4	0·217	1·90
,, ,, 6.15 ,, ...	19·9	479·3	0·094	1·40
,, ,, 7.8 ,, ...	132	481·0	0·127	
,, 13th, 11.45 a.m....	17·4	469·4	0·079	1·28
,, ,, 12.20 ,, ...	132	470·5	0·101	
,, 15th, 11.20 ,, ...	16·2	472·0	0·066	1·36
,, ,, 12.10 ,, ...	132	472·7	0·134	
,, 16th, 11.15 ,, ...	16·3	209·0	0·084	1·29
,, ,, 12·5 p.m....	132	213·0	0·102	
,, ,, 4·18 ,, ...	237	479·9	0·196	1·33

The approximate agreement of the dissociation figures for 132° over the four days is strong evidence that these figures themselves are correct, and the agreement between the actual volumes and those calculated from electrical measurements shows that most of the helium has been occluded, and that it does not interfere with the ratio.

Throughout this research the actual volumes have been measured at temperatures varying between 10° and 20°, and have been corrected to 0°. The figures just quoted show conclusively that the expansion of the emanation is abnormal; for small differences of temperature, however, Gay-Lussac's law may be assumed to hold good.

In dealing with the figures given in the preceding tables it was necessary to be able to estimate the part played by adsorption or occlusion of gas by the walls of the tube; special experiments were therefore made with this object.

(6) *The Adsorption or Occlusion of Helium, Carbon Dioxide, Hydrogen, and Oxygen by Glass and Silica.*—For these experiments the same apparatus was used; the reservoir H was never raised, but after admitting gas to the whole apparatus the tap K was closed and mercury was forced into the capillary by raising the reservoir M. By lowering the level of the mercury below the fork and opening the tap K some gas could be removed if necessary.

Experiment VII.—After the deposit, supposed to be radium *D*, had been observed in tube A, it was heated with a measured quantity of oxygen; had it formed an oxide there should have been a measurable decrease in volume. In twenty-four hours the volume decreased from 1·782 to 1·579 cub. mm.; this is equal to 11·4 per cent. On warming the tube again the volume returned to 1·782 cub. mm.

Experiment VIII.—Tube B was tested with helium before emanation was introduced; 1·165 cub. mm. contracted to 1·113 cub. mm. in two hours—a loss of 4·5 per cent. After twenty-four hours the final volume was 1·090 cub. mm., or 6·4 per cent. contraction. More helium was then introduced into the same tube; in eighteen hours 7·933 cub. mm. contracted to 7·903 cub. mm.

Experiment IX.—After two quantities of emanation had been measured in tube B a measured quantity of carbon dioxide was introduced. In two hours 3·265 cub. mm. had contracted to 3·218, implying an adsorption of only 1·4 per cent.

Experiment X.—The silica tube was tested with helium previous to its use with emanation. A considerable contraction occurred;

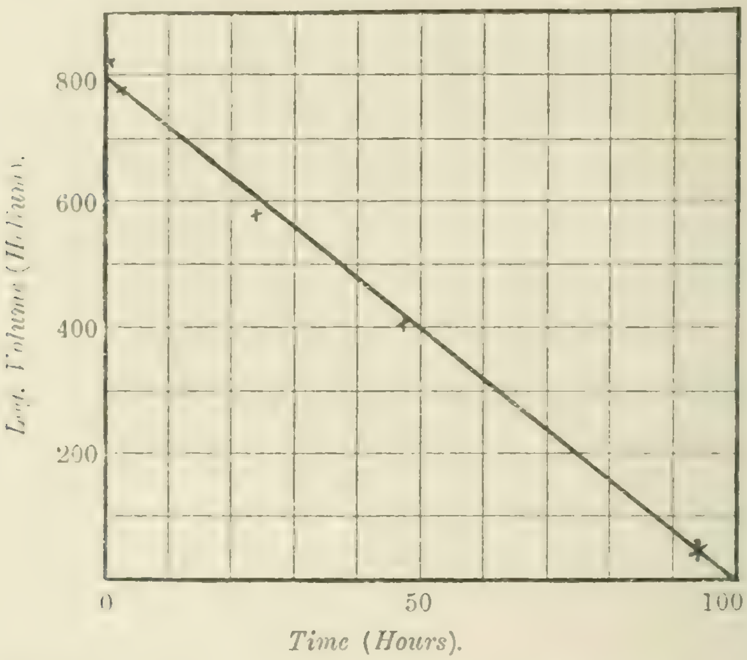
as the decrease is proportional to the surface exposed the results give a logarithmic curve.

Time, in hours.	Volume, cub. mm.	Log volume.	No. of observations.	Limits of P.V., mm.	Decrease, per cent.
0·0	0·665	823	5	509·0—556·9	—
2·25	0·598	777	5	458·1—506·8	10·7
23·75	0·377	576	4	281·1—323·0	43·3
47·25	0·254	405	5	196·8—212·9	61·8
94·5	0·110	041	4	86·3— 90·7	83·4

In Fig. 4 the logarithms of the volumes are plotted against time; the result is a straight line within the limits of error.

Experiment XI.—After experiments V. and VI. with emanation had been completed the tube was again tested with helium; the volume remained unaltered. A tube which had been made at the same time was then tested; in twenty-two hours there was a decrease in volume of 2·5 per cent. After heating the tube in the blowpipe for a quarter of an hour the volume of gas increased considerably, showing that the tube had occluded gas; this gas was not reabsorbed.

FIG. 4.



Experiment XII.—A new silica tube of greater diameter, with a correction for capillarity of 18·1 mm., was sealed to the apparatus; it was evacuated and strongly heated; helium was then introduced. In twenty hours 0·5 per cent. had disappeared. The tube was then heated in the blowpipe for twenty minutes and pumped empty at the same time, and a fresh quantity of helium was introduced; in four hours the contraction was 1·2 per cent.; in twenty-four hours 2 per cent.; and after three days 2·7 per cent.

Experiment XIII.—In order to try to reproduce the first conditions, when the rapid absorption of helium took place, the tube used in experiment VI. was reopened, cleaned with a mixture of potassium dichromate and sulphuric acid, washed out thoroughly with water, and dried in a current of dry air; it was then re-sealed, fixed to the apparatus, pumped empty, and heated in the blowpipe for a quarter of an hour. After the tube had cooled for an hour helium was admitted; during the first ten minutes 1 per cent. of the volume disappeared; in an hour 3 per cent.; and in eighteen hours 5·5 per cent. There was no further change.

Experiments XIV., XV., and XVI.—The tube was heated in the blowpipe for a quarter of an hour, being exhausted all the time. After it had cooled for an hour carbon dioxide was admitted; in half an hour less than 0·5 per cent. had disappeared; and in eighteen hours 2·1 per cent. Similar experiments were carried out with hydrogen and with oxygen. Hydrogen lost 2·5 per cent. of its volume in eighteen hours and oxygen 1·1 per cent. in the same time.

(7) *Discussion of Experimental Results.*—From the experiments just described it may be concluded that the adsorption of all gases except helium is unimportant under ordinary conditions. Experiment X. shows, however, that a silica-glass tube may absorb or occlude helium at atmospheric temperature; after treatment with emanation this power is lost. We have not succeeded in discovering the conditions which favour occlusion; but if the helium is derived from emanation, or if the tubes are bombarded by *X*-rays in presence of a gas, the helium or that gas is absorbed. Campbell Swinton has shown (*Proc. Roy. Soc.*, 1907, **79**, 134) that in the latter case the helium is occluded as bubbles in the glass, which can be detected microscopically. It has been suggested that the enormous velocity of the particles proceeding from the emanation produces a similar effect, causing the absorption of the helium as fast as it is produced. The detailed results of experiments I. to VI. show (especially experiment III.) a remarkable parallelism between the observed volumes and those calculated from electrical data, if half the initial volume be taken as the starting-point; but in all cases the observed volume gradually exceeds the calculated volume; in experiment I., not only is the contraction less than it should be, but an actual expansion has been observed. We may suppose that the tube gradually becomes more and more impervious to helium; it is possible that the coating of radium *D* which is deposited on the surface acts as a protective shield against the

bombardment. Since the emanation produces three or four times its volume of helium, when absorption ceases, the volume necessarily increases.

This parallelism emphasises the difference between the gradual decay and the initial change, which is practically complete in one and a quarter hours. It is evident that the initial change cannot be ascribed to adsorption or occlusion, for a gas, carbon dioxide, resembling the emanation to some extent in the temperature at which it condenses, is practically unabsorbed. If, then, adsorption be discarded as insufficient to account for the rapid decrease of volume, two possible explanations remain: (1) The emanation decomposes into a solid, which deposits on the walls of the tube, leaving a gas which occupies only half the original volume; or (2) the monatomic gas, Em_1, becomes diatomic, Em_2, with consequent halving of volume.

The first hypothesis is extremely improbable. For such a decomposition should take place under all conditions; it should not produce a sudden decrease of volume when the emanation is separated from admixed gases. Again, it has been shown that the emanation does deposit a solid, which goes through successive stages as radium *A*, *B*, *C*, *D*, &c. This is formed according to the normal rate of decay. Were the hypothesis correct it would be deposited by the second gas, Em_2, it is certainly not the hypothetical solid referred to. Thirdly, if an appreciable quantity of solid were deposited, it should have immediate effect in preventing the occlusion of helium; but helium is almost completely occluded for four or five days.

The second hypothesis agrees with all the known facts; the change from Em_1 to Em_2 involves an exponential curve, and that has been realised. Again, a rise of temperature should cause dissociation, and that has been observed; at 80°, 90 per cent. was dissociated, and at 132° only 40 per cent. Such a result is unexpected, yet not in disagreement with the hypothesis. Rutherford's sequence would then become $Ra - Em_1 - Em_2 - RaA - RaB - RaC$, &c.

The curves in Fig. 2 may be more easily understood by considering the rate of formation of Em_2 from Em_1; this is obtained by subtracting the volume at time *t* from the initial volume. The figures in the fourth column are calculated by the equation

$$V_t/V_\infty = 1 - e^{\lambda t},$$

λ having the same significance as before; its value is 0·0764, and V is taken as 0·102.

Time, in minutes.	Total volume, cub. mm.	Volume of Em_2, cub. mm.	Calculated volume, cub. mm.
0	0·187	0·000	0·000
7	0 147	0 040	0·042
11	0·129	0·058	(0·058)
14	0·118	0·069	0·067
16·5	0·110	0·077	0·073
20	0·104	0·083	0·080
25	0·101	0·086	0·087
36	0·092	0·095	0·096
45	0·090	0·097	0·099
64	0·087	0·100	0·101
75	0·085	0 102	0·1017

The agreement would be good for measurements of large gas-volumes; considering the smallness of the actual volumes measured it is wonderfully close.

Rutherford and others have shown that whilst radium *A*, *B*, and *C* have a life-period of only a few hours, radium *D* has a half-life-period of forty years. We believe that the brown, semi-metallic deposit, frequently seen during these experiments, can consist only of this substance. When a tube containing it is ignited, the portion containing it glows, whilst the portion which has been exposed only to contact with mercury remains non-luminous. This substance does not readily give an oxide; we are examining it more carefully.

The Life-period of Radium.—On the assumption that one atom of radium produces one atom of emanation, and that both gases are monatomic, Ramsay and Soddy found from their two experiments that the average life of the radium atom was respectively 1,050 and 1,150 years. In the first experiment they accepted the volume 0·027 cub. mm., measured after twenty-four hours, as correct, calculating the original volume from it; in the second the original volume was taken; it was much smaller, for pumping had been carried to a further point and emanation had been doubtless removed.

We have given reasons for believing that the original volume is correct for the monatomic gas; the mean of three fairly concordant experiments from 87·7 milligrams of metallic radium as bromide and sulphate was 0·310 cub. mm. of emanation in 3·86 days. The method of calculation is identical with that of Ramsay and Soddy; and in view of the importance of the result it may be recapitulated here.

From 1 gram of radium there will be produced in 3·86 days 3·535 cub. mm. of emanation. If Q is the equilibrium quantity of emanation (produced after infinite time), Q_t the quantity produced in time *t*, measured in days, and λ a constant representing the proportion of emanation changing per day, then

$$Q_t/Q = 1 - e^{-\lambda t},$$

and $\lambda = 0{\cdot}1796$. Using this formula, the amount of emanation formed in one day is found to be 1·162 cub. mm. Since 1 gram of radium, on the assumption that it is a monatomic gas, occupies $(2 \times 11{\cdot}2)/225 = 0{\cdot}1$ litre $= 10^5$ cub. mm., the proportion of radium changing per day is $1{\cdot}162 \times 10^{-5}$. The average life will be the reciprocal of this number,

$$\frac{10^5}{1{\cdot}162} \text{ days, or 236 years.}$$

This is totally at variance with the number obtained by Rutherford and others from theoretical considerations.

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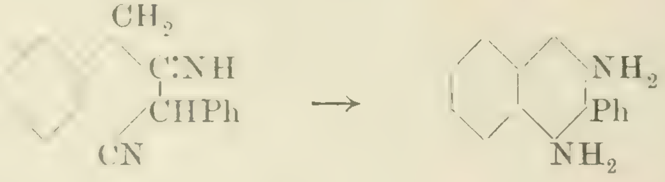
CXIX.—*Some Derivatives of 2-Phenyl-1 : 3-naphthylenediamine. Part I.*

By NORMAN LEES and JOCELYN FIELD THORPE.

IN a communication dealing with the formation and reactions of imino-compounds (Part II, Atkinson and Thorpe, Trans., 1906, **89**, 1930 *et seq.*) a method is described by which 2-phenyl-1 : 3-naphthylenediamine (II) can be prepared in large quantities by the action of cold concentrated sulphuric acid on β-imino-α-cyano-$\alpha\gamma$-diphenylpropane (I):

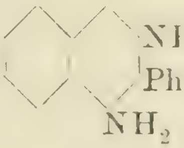


(I.) (II.)

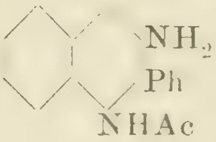
Since this base is the only member of its class which has yet been prepared, we have subjected it to a complete examination in order mainly to determine the influence of the benzene nucleus on the two adjacent amino-groups in the naphthalene ring. If the formula (II) is examined, it will be seen that the phenyl group, placed as it is between the two amino groups, must affect their basicity equally. The α-amino-group is attached, however, to the carbon atom adjacent to the benzene nucleus which forms part of the naphthalene ring, and hence if this nucleus affects the basicity of an α-amino-group, it will cause the α-amino group in 2-phenyl-1 : 3-naphthylenediamine to be much less basic than the β-amino-group.

Our experiments show that this is in fact the case, and that the α-amino-group in 2-phenyl-1 : 3-naphthylenediamine is much less basic than the amino-group in the β-position. Thus the β-amino-group reacts first in salt formation, diazotisation, and in acetylation, enabling therefore a series of derivatives to be prepared in the formation of which the β-amino-group alone takes part; on the other hand, since this group can be readily protected by acetylation, another series can be formed from the amino-group in the α-position.

As soon as it was apparent that the two amino-groups reacted differently, the chief problem which had to be solved was the position of the substituent groups and the identity of the amino-group entering into the various reactions. The compound which was mainly instrumental in enabling us to settle these points was a monoacetyl derivative which can be prepared by the action of acetic anhydride on the diamino-base. The product of this interaction is an acetyl acetate, the preparation and properties of which were described in a former communication (*loc. cit.*, p. 1935). When treated with mineral acids, this acetyl acetate yields the salt of a monoacetyl derivative from which the monoacetyl base can be readily prepared by the usual methods. The monoacetyl derivative may of course possess either of the formulæ (III) or (IV):



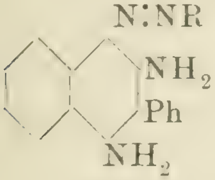
(III.)



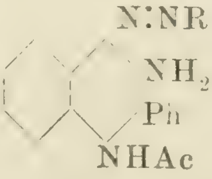
(IV.)

The proof that the acetyl group is in the β-position and that the formula of the compound is represented by (III) is as follows.

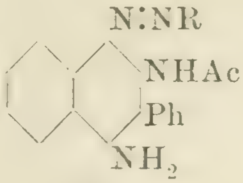
2-Phenyl-1 : 3-naphthylenediamine readily reacts with diazonium salts, forming azo-compounds of the type (V):



(V.)



(VI.)



(VII.)

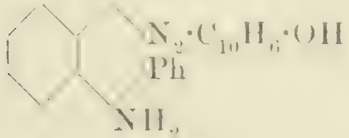
These azo-compounds readily form salts with strong mineral acids, the amino-group yielding the salt being that in the position (4) in respect to the azo-group. When treated with acetyl chloride, the azo-compounds give well-defined acetyl derivatives which do not form salts with mineral acids, and which must therefore possess a constitution represented by (VI).

Moreover, the monoacetyl derivative of 2-phenyl-1 : 3-naphthylenediamine mentioned above, formula (III) or (IV), also combines readily with diazonium salts yielding acetyl derivatives of azo-compounds which readily form salts with mineral acids. These acetylazo compounds must therefore possess a constitution represented by (VII), and hence the formula of the monoacetyl derivative of 2-phenyl-1 : 3-naphthylenediamine must be represented by (III). Having in this way established the formula of the monoacetyl derivative, it was an easy matter to determine the formulæ of the various azo-compounds derived both from it and from the diamino-base itself, as well as of the two aminonaphthols derived by the replacement of one or other of the amino-groups of 2-phenyl-1 : 3-naphthylenediamine by hydroxyl.

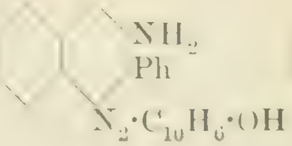
The action of nitrous acid on 2-phenyl-1 : 3-naphthylenediamine recalls the behaviour of *m*-phenylenediamine under similar conditions, for if the hydrochloride of the base containing the usual excess of hydrochloric acid is titrated with standard sodium nitrite solution a brown colouring matter is formed which is closely analogous to Bismarck-brown both in appearance and constitution. If, however, the base is dissolved in concentrated hydrochloric acid and then titrated with standard sodium nitrite solution at 0°, the solution remains clear and an amount of nitrite corresponding with that required for the diazotisation of one amino-group is absorbed. The reaction evidently stops here, for even if the strong acid solution is left in contact with excess of nitrous acid for many hours no further quantity is taken up.

Thus only one amino-group of 2-phenyl-1 : 3-naphthylenediamine is acted on by nitrous acid, and that this is the one which is in the *β*-position is shown by the following considerations.

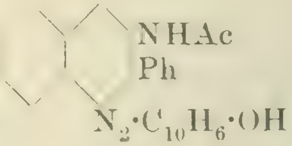
The diazonium salt formed by the diazotisation of the base in concentrated hydrochloric acid solution cannot be made to combine with amines, since it is not possible, apparently, to replace the excess of hydrochloric acid by acetic acid without causing the formation of the brown colouring matter to which reference has already been made. No combination takes place between an amine and the strongly acid solution of the diazonium salt, but if the latter is poured into a solution of *β* naphthol containing excess of sodium hydroxide an azo-compound is formed and can be isolated. The formula of this azo-compound must either be (VIII) or (IX):



(VIII.)



(IX.)



(X.)

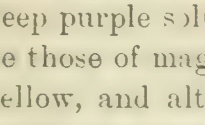
That its constitution is represented by (VIII), and that therefore it is the *β*-amino group of 2-phenyl-1 : 3-naphthylenediamine which is diazotised, is shown by the fact that the azo-compound which is prepared by the diazotisation of the monoacetyl derivative (III) and its combination with *β*-naphthol, and which must therefore possess the formula (X), yields on hydrolysis an azo compound which is quite different from that prepared from the diazonium salt of the diamino base.

The azo-compounds derived from the β-amino-group of 2-phenyl-1 : 3-naphthylenediamine can therefore be prepared by the direct diazotisation and subsequent coupling of the base itself, whereas those derived from the α-amino-group can be prepared from the monoacetyl derivative, the true azo-compound being readily obtained by the hydrolysis of the acetyl derivative thus formed.

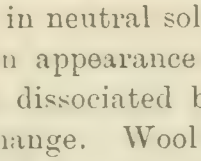
The azo-compounds formed from 2-phenyl-1 : 3-naphthylenediamine either by coupling it with diazonium salts or by diazotising the base (or its monoacetyl derivative) and coupling the diazonium salt thus produced with amines and phenols show that the presence of the phenyl group has little effect on the colour of the azo-compounds and that the shades of these compounds do not differ appreciably from those of the corresponding derivatives of 1 : 3-naphthylenediamine. The presence of the phenyl group has, however, a marked effect on the stability of salts of azo-compounds derived from the base and diazonium salts, causing them to be readily dissociated by water and stable only in the presence of dilute acid. This property, which gives rise to certain peculiarities, is well illustrated by the azo-compound formed from the base and diazotised *p*-nitroaniline. This azo-compound yields deep purple solutions in neutral solvents and its crystals closely resemble those of magenta in appearance; the hydrochloride is, however, yellow, and although dissociated by water, dissolves in dilute hydrochloric acid without change. Wool boiled in the yellow solution of this salt is dyed yellow, but on washing with water is changed to deep purple owing to the decomposition of the salt on the fibre.

Further evidence regarding the greater reactivity of the β-amino-group as compared with that in the α-position in 2-phenyl-1 : 3-naphthylenediamine is furnished by the behaviour of the base on salt formation. When 2-phenyl-1 : 3-naphthylenediamine is titrated with decinormal hydrochloric acid an amount of acid is absorbed corresponding with the formation of a dihydrochloride.

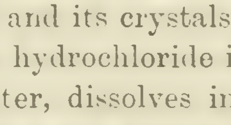
The solution of the salt prepared in this way is converted, on heating in a sealed tube, into 1 : 3-dihydroxy-2-phenylnaphthalene (XI).



(XI.)



(XII.)



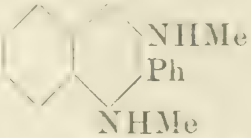
(XIII.)

If, however, the base is treated with a sufficient quantity of standard hydrochloric acid to form the monohydrochloride, it passes into solution and a definite monohydrochloride can be obtained by evaporation. An aqueous solution of this basic salt when heated in a sealed tube yields an aminonaphthol the formula of which must be represented by (XII) for the following reasons.

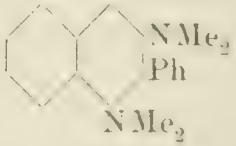
The monoacetyl derivative of 2-phenyl-1 : 3-naphthylenediamine (III) can be readily diazotised at 0° and the solution of the diazonium salt thus obtained, which shows no tendency to combine with itself, forms, when boiled, an acetyl derivative of an aminonaphthol, nitrogen being at the same time eliminated. This compound is converted on hydrolysis into an aminonaphthol which from its mode of formation must have a constitution represented by (XIII) and which is quite different from the aminonaphthol derived from the monohydrochloride, which must therefore possess a constitution represented by (XII).

It is therefore evident from these experiments that the *β*-amino-group in 2-phenyl-1 : 3-naphthylenediamine is more basic than the *α*-amino-group, since it is the one first acted on in salt formation, diazotisation, and acetylation.

The methylation of 2-phenyl-1 : 3-naphthylenediamine was effected with the aid of methyl sulphate and an excellent yield of the *sym*-dimethyl derivative (XIV) was obtained under the conditions described in the experimental portion:



(XIV.)



(XV.)

This base exists in three well-defined forms, two of which are evidently physical isomerides and can be obtained from the same solution under different conditions of crystallisation; the third is, however, not a physical isomeride, but we have not as yet been successful either in determining the relationship between this form and the other two or in ascertaining the conditions under which it passes into them. For the sake of convenience we have termed the dimorphous variety the *α*-form and the third variety the *β*-form. The *α*-form is produced when the base is dissolved in methyl alcohol, treated with methyl sulphate and the solution immediately shaken with sodium hydroxide solution. No trace of the *β*-form could be isolated from this product, but it occurs as the chief product when the diamino-base is treated with methyl sulphate at 100° and the excess of sulphate subsequently destroyed by hot water. In this case no trace of the *α*-form could be isolated. Both forms are disecondary bases and yield dinitrosoamines with nitrous acid, which, although melting very near together (175° and 179°), seem to crystallise in different forms. In the formation of the dinitrosoamine the *β*-form reacts at once, whereas the *α*-form reacts very slowly and it is necessary to leave a solution of the hydrochloride of the base containing the requisite excess of hydrochloric acid for several hours in contact with sodium nitrite solution before the precipitation of the dinitrosoamine is complete.

When either form of 2-phenyl 1 : 3-naphthylenedimethyldiamine is further methylated the tetramethyl derivative (XV) is produced. Nitrous acid is without action on this compound at 0°, but at 5° interaction slowly takes place with the formation of a well-defined nitroso-derivative.

In view of the work by Morgan and his collaborators on the interactions of aromatic metadiamines and diazo-compounds, a summary of which has been given recently (Trans., 1907, **91**, 370), it is interesting to note the marked influence which the methylation of the amino-groups in 2-phenyl-1 : 3-naphthylenediamine has on the capacity of the bases formed for yielding azo-compounds. In this respect, although the bases still contain a free para-position into which the azo-group can enter, yet in many respects they resemble the di-para substituted *m*-diamines described by Morgan.

Thus the *sym*-dimethyl derivative reacts slowly and very incompletely with diazonium salts yielding true azo-compounds, whereas the tetramethyl derivative is quite unacted on even by the diazonium salt derived from *p*-nitroaniline. The formation of diazoamino-compounds in the case of the secondary base was not observed.

*Preparation of 2-phenyl-*1 : 3-*naphthylenediamine.*

The preparation of this base in large quantities was effected in the following manner, which was found to be more convenient and more easily controlled than the method given in the previous paper (Trans., 1906, **89**, 1930): 11·5 grams of sodium were covered with freshly distilled xylene in a small flask, and heated on the sand-bath until the sodium had melted, when the metal was brought into a fine state of division by vigorously shaking the flask. The whole was then transferred to a larger flask, mixed with 300 c.c. of freshly distilled xylene, and then with 117 grams of phenylacetonitrile. The sodium rapidly dissolved on adding the nitrile, considerable heat being generated, which necessitated the temperature being controlled by means of running water. After the whole of the sodium had passed into solution the product was heated on the water-bath for fifteen minutes, at the end of which time the contents of the flask had become solid owing to the separation of the sodium compound of β-imino-α-cyano-$\alpha\gamma$-diphenylpropane, $CHNaPh\cdot C(:NH)\cdot CHPh\cdot CN$. It is essential that this sodium compound should be precipitated; otherwise the heating on the water-bath must be continued until the precipitation takes place. Should no sodium compound separate even on further heating it is probable that the temperature during the solution of the sodium has been allowed to become too high, and the product will be found to consist for the most part of cyanbenzyline (Trans., 1906, 89, 1931), a compound which will have been formed by the condensation of the sodium derivative of β-imino-α-cyano-αγ-diphenylpropane and unchanged phenylacetonitrile.

A large quantity of dilute hydrochloric acid was added after the precipitation of the sodium compound had taken place and the xylene solution separated in a funnel, the xylene extract being subsequently washed to remove the last traces of alkali. The product was then subjected to distillation in a current of steam until the whole of the xylene and unchanged nitrile had passed over, when the residual oil was extracted with ether, the ethereal extract being washed with dilute hydrochloric acid to remove cyanbenzyline, dried and evaporated free from ether. The thick liquid which remained was, without further purification, dissolved in three times its volume of concentrated sulphuric acid, the mixture being well cooled during the process.

After all had dissolved, the strong acid solution was poured in a thin stream into a large volume of water, and the solution of the sulphate thus formed filtered to remove insoluble impurities. In some experiments a considerable quantity of resinous matter separated when the sulphuric acid solution was poured into water. This was always due to the presence of cyanbenzyline in the condensation product, and also to a certain extent to the presence of α-cyano-β-keto-αγ-diphenylpropane (compare Trans., 1906, 89, 1933). The resinous product therefore consisted of a mixture of the sulphate of cyanbenzyline and a compound which is formed by the action of concentrated sulphuric acid on the ketone, the nature of which has not yet been determined.

The filtrate on being rendered alkaline by ammonia deposited the base as a thick oil which set to a resin on cooling. This resin on recrystallisation from alcohol yielded the pure base melting at 116°, the properties of which have already been described.

Diazotisation of 2-Phenyl-1 : 3-naphthylenediamine.

In its behaviour towards nitrous acid 2-phenyl-1 : 3-naphthylenediamine closely resembles *m*-phenylenediamine. Thus when a solution of the dihydrochloride of the base containing excess of dilute hydrochloric acid is treated with a solution of sodium nitrite a brown colouring matter separates. Like Bismarck-brown this compound is evidently a mixture of two or more substances, and it was not found possible to isolate a definite compound from the mixture. When a large excess of concentrated hydrochloric acid is present, however, the solution of the hydrochloride can be titrated with standard sodium nitrite at 0° without the formation of this brown colouring matter, and the solution, although becoming deep yellow, remains clear. A quantitative experiment showed that an amount of nitrous acid sufficient to diazotise one amino-group had been taken up, and that the second amino-group remained unacted on even when left in contact with excess of nitrous acid for a considerable time.

The solution of the diazonium salt thus obtained could not be combined with amines, since, when any attempt was made to neutralise the large excess of hydrochloric acid by means, for example, of sodium acetate, the precipitation of the brown colouring matter already referred to always took place. In the strongly acid solution of the diazonium salt itself there was apparently no tendency at all to form azo-compounds with amines, but when the solution of the salt was run into a solution of β-naphthol containing a large excess of sodium hydroxide a reddish-purple precipitate was formed. It was collected and recrystallised from benzene, in which solvent it is only sparingly soluble, but separates from a large quantity in deep purple microscopic needles, which melt at 270°.

0·2115 gave 19·7 c.c. of nitrogen at 20° and 770 mm. N = 10·89.
$C_{26}H_{19}ON_3$ requires N = 10·8 per cent.

This compound is therefore 1-*amino*-2-*phenylnaphthalene*-3-*azo*-β *naphthol*, $NH_2 \cdot C_{10}H_5Ph \cdot N_2 \cdot C_{10}H_6 \cdot OH$, since, as already mentioned in the introduction, there is no doubt that it is the amino-group in the β-position in 2-phenyl-1 : 3-naphthylenediamine which undergoes diazotisation. The azo-compound is insoluble in dilute acids or alkalis, but dissolves in concentrated hydrochloric acid, forming a salt which is dissociated by water. With concentrated sulphuric acid the azo-compound gives a deep violet-blue solution.

After the strongly acid solution of the diazonium salt had stood at 0° for 24 hours, it was found that a pale brown crystalline precipitate had separated which was collected and dried on a porous plate in a desiccator over potash. From its reactions this substance would appear to be the free diazonium chloride. It explodes violently at about 120°, and evolves nitrogen when boiled with concentrated hydrochloric acid. When boiled with water it is partially decomposed with evolution of nitrogen and partially transformed into the brown condensation product. It is stable in moderately concentrated hydrochloric acid, and the solution thus formed exhibits all the reactions of the diazonium salt of the diamino-base. Owing to its explosive nature we were unable to obtain any satisfactory figures on analysis, and attempts made to determine the amount of nitrogen evolved on boiling with hydrochloric acid always gave figures which were about 2 per cent. too low, owing doubtless to the impossibility of entirely preventing the formation of the brown condensation product. When boiled with ethyl alcohol the diazonium salt yielded acetaldehyde, but all attempts to isolate the corresponding monoamine were unsuccessful, the product being a resin from which no definite substance could be isolated. An investigation of the product formed on the elimination of nitrogen from the diazonium salt on boiling with hydrochloric acid also yielded negative results, since in this case also the product was a resin from which no crystalline substance could be prepared.

Combination of 2-*Phenyl*-1 : 3-*naphthylenediamine with Diazonium Salts.*

The combination of diazonium salts with 2-phenyl-1 : 3-naphthylenediamine takes place in the position (4) in the naphthalene ring. The combination is effected very readily, usually in dilute acetic acid solution, and the yields of the azo-compounds are practically quantitative. The influence of the phenyl group causes the salts of the azo-bases to be unstable in aqueous solution; they are, however, stable in the presence of dilute mineral acids.

4-*Benzeneazo*-2-*phenyl*-1 : 3-*naphthylenediamine*,

$$(NH_2)_2C_{10}H_4Ph\cdot N_2\cdot Ph,$$

was prepared by adding a diazotised solution of 0·45 gram of aniline, from which the excess of hydrochloric acid had been eliminated by means of sodium acetate, to a solution of 1 gram of the base dissolved in dilute hydrochloric acid. On mixing the solution the free azo-compound separated as a bright red precipitate. It was purified by crystallisation from a mixture of alcohol and benzene, and obtained in red needles melting and decomposing at 210°:

0·1438 gave 21·0 c.c. of nitrogen at 10·7° and 731 mm. N = 16·74.

$C_{22}H_{18}N_4$ requires N = 16·6 per cent.

The azo-compound is soluble in hot dilute hydrochloric acid, forming a deep orange-red solution, from which on cooling the *hydrochloride*, $C_{22}H_{18}N_4,HCl$, is precipitated in orange-yellow needles:

0·2109 gave 0·0803 AgCl. Cl = 9·38.

$C_{22}H_{18}N_4,HCl$ requires Cl = 9·5 per cent.

The salt is dissociated by boiling water, but can be dissolved in dilute hydrochloric acid without change.

4-*Benzeneazo*-1-*acetylamino*-3-*amino*-2-*phenylnaphthalene* was prepared in order to compare it with the corresponding 4-benzeneazo-3-acetylamino-1-amino-2-phenylnaphthalene which was formed by the combination of the monoacetyl derivative of 2-phenyl-1 : 3-naphthalenediamine with benzenediazonium chloride (see page 1295). The azo-compound was treated with excess of acetyl chloride, when a vigorous reaction ensued and hydrogen chloride was evolved. After the reaction had been completed by warming on the water-bath, the acetyl derivative, which remained undissolved, was isolated and recrystallised from alcohol yielding brilliant red prisms with green metallic reflex which decomposed at 200°:

0·2298 gave 28·8 c.c. of nitrogen at 16·5° and 774 mm. N = 14·85.

$C_{24}H_{20}ON_4$ requires N = 14·7 per cent.

The acetyl derivative does not form salts with acids.

4-α-*Naphthaleneazo-2-phenyl-*1 : 3-*naphthylenediamine*,

$(NH_2)_2C_{10}H_4Ph\cdot N_2\cdot C_{10}H_7(\alpha)$,

is precipitated as a red-brown powder when a solution of 0·61 gram of α-naphthylamine, diazotised in the usual way, is added to a solution of 1 gram of the base in dilute hydrochloric acid. When recrystallised from alcohol and benzene it forms red-brown needles which melt at 218°:

0·1885 gave 23 c.c. of nitrogen at 13° and 760 mm. N = 14·42.

$C_{26}H_{20}N_4$ requires N = 14·4.

The azo-compound dissolves in hot dilute hydrochloric acid forming a red-brown solution from which the hydrochloride is deposited on cooling in slender brown needles; it is only sparingly soluble in hot dilute hydrochloric acid and is dissociated by boiling water.

4-p-*Nitrobenzeneazo-2-phenyl-*1 : 3-*naphthylenediamine*,

$(NH_2)_2C_{10}H_4Ph\cdot N_2\cdot C_6H_4\cdot NO_2$.

The hydrochloride of this compound is precipitated as an orange-yellow powder on adding a solution obtained by diazotising 0·59 gram of *p*-nitroaniline to a solution of 1 gram of the base in dilute hydrochloric acid.

On filtering this precipitate and washing it with water the orange-coloured salt is dissociated and is transformed into the deep purple base, which can be purified by recrystallisation from a mixture of alcohol and benzene; it is thus obtained in large prisms with deep green metallic reflex which appear purple by transmitted light and melt at 210—211°:

0·1641 gave 25·9 c.c. of nitrogen at 19° and 760 mm. N = 18·15.

$C_{22}H_{17}O_2N_5$ requires N = 18·27.

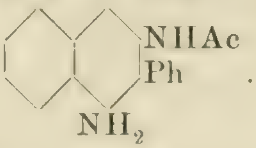
The base dissolves in hot dilute hydrochloric acid, forming a yellow solution from which the *hydrochloride*, $C_{22}H_{17}O_2N_5,HCl$, separates, on cooling, in yellow needles:

0·2919 gave 0·0984 AgCl. Cl = 8·31.

$C_{22}H_{17}O_2N_5,HCl$ requires Cl = 8·4 per cent.

Wool dyed in a solution of the hydrochloride in dilute hydrochloric acid is coloured yellow, but the dyed fabric is changed to a deep purple on washing with water owing to the decomposition of the salt on the fibre.

*Monoacetyl Derivative of 2-Phenyl-*1 : 3-*naphthylenediamine,*



In a former communication (Trans., 1906, **89**, 1935) it was pointed out that when 2-phenyl-1 : 3-naphthylenediamine was boiled with acetic anhydride the product consisted of a stable acetyl acetate, and not of the diacetyl derivative, which it was ultimately found could only be prepared from the base by the action of acetyl chloride. On boiling this acetyl acetate with dilute hydrochloric acid until all has passed into solution, the monoacetyl derivative of the above formula can be obtained on rendering the solution alkaline. The proof of the constitution of this substance is dealt with in the introduction.

The Acetyl Acetate.—The following method was adopted in order to prepare this compound in large quantities: 50 grams of the base were dissolved in 300 grams of freshly distilled acetic anhydride and heated in a Geissler flask on the sand-bath for two hours. At the end of this time the dark-coloured liquid was transferred to a distilling flask and the excess of the anhydride distilled off, the residue being poured into a glass dish and allowed to crystallise. The crude product was then spread on a porous plate and, when dry, recrystallised once from alcohol. In this way the compound was obtained sufficiently pure for further use.

The Monoacetyl Derivative.—The transformation of the acetyl acetate into this compound was effected as follows: the acetyl acetate was boiled in a flask with dilute hydrochloric acid until all had dissolved, an operation which usually took from ten to fifteen minutes, when the solution, after being filtered, was made alkaline with ammonia and the monoacetyl derivative which then separated was isolated by filtration. Owing to the fact that the hydrochloride of the monoacetyl derivative is very insoluble in dilute hydrochloric acid, it is necessary to wash thoroughly any insoluble matter which may have remained after the acetyl acetate has been boiled for the necessary time, since if the acid used is too strong a considerable quantity of this hydrochloride will remain undissolved. Like many of these derivatives of 2-phenyl-1 : 3-naphthylenediamine, the monoacetyl derivative is frequently precipitated by alkalis from the solution of its hydrochloride in the form of a resin, but the resin readily dissolves in hot benzene or ethyl alcohol and the solution, on cooling, deposits the pure monoacetyl derivative in small glistening plates, sometimes slightly yellow in colour, which melt at 220°:

0·2155 gave 19·0 c.c. of nitrogen at 15° and 775 mm. N = 10·52.
$C_{18}H_{16}ON_2$ requires N = 10·2 per cent.

The *hydrochloride*, $C_{18}H_{16}ON_2,HCl$, is best prepared by dissolving the base in hot dilute hydrochloric acid and allowing the solution to cool, when the salt separates as a microcrystalline powder. It is readily soluble in cold water, but is practically insoluble in hydrochloric acid:

0·2721 gave 0·1222 AgCl. Cl = 11·07.
$C_{18}H_{16}ON_2,HCl$ requires Cl = 11·2 per cent.

The *benzylidene* derivative, $NHAc\cdot C_{10}H_5Ph\cdot N:CHPh$, is formed when a benzene solution of the base is mixed with a benzene solution of benzaldehyde and the mixture warmed, the condensation product separating as a pale yellow precipitate on cooling the solution. It was purified by recrystallisation from benzene and was obtained in pale yellow needles melting at 188—189°:

0·1877 gave 12·7 c.c. of nitrogen at 14·0° and 765 mm. N = 8·0.
$C_{25}H_{20}ON_2$ requires N = 7·7 per cent.

Diazotisation of the Monoacetyl Derivative.

When a solution of the hydrochloride of the monoacetyl derivative containing excess of hydrochloric acid is titrated with a standard solution of sodium nitrite in ice-cold solution the requisite amount of nitrous acid required for the diazotisation of the one amino-group is absorbed and the solution, although becoming slightly yellow, remains quite clear.

The diazonium salt thus produced can be combined with any second compound and the azo-compounds formed can, on treatment with sodium hydroxide solution, be converted into the azo-compounds of 2-phenyl-1 : 3-naphthylenediamine.

One typical azo-compound chosen to illustrate these properties was that formed by the condensation of the diazonium salt with β-naphthol. That this compound should on hydrolysis yield an azo-compound differing from that derived by the direct diazotisation of 2-phenyl-1 : 3-naphthylenediamine in combination with β-naphthol is proof that in the latter case it is the β-amino-group which is diazotised. This point is dealt with at length in the introduction.

3-*Acetylamino-2-phenylnaphthalene*-1-*azo*-β-*naphthol*,
$NHAc\cdot C_{10}H_5Ph\cdot N_2\cdot C_{10}H_6\cdot OH$.
—This azo-compound may be prepared as follows: 2·2 grams of the

monoacetyl derivative are dissolved in dilute hydrochloric acid, the solution cooled with ice and titrated with standard sodium nitrite solution until the presence of free nitrous acid can be detected by starch and potassium iodide paper. Sodium acetate in excess is then added to the clear diazo-solution and the mixture poured into a solution of 0·52 gram of β-naphthol in dilute aqueous sodium hydroxide. A red compound is at once precipitated, which on recrystallisation from glacial acetic acid is obtained in small red needles melting at 285°.

0·2439 gave 21·2 c.c. of nitrogen at 15° and 756 mm. N = 10·01.
$C_{28}H_{21}O_2N_3$ requires N = 9·8 per cent.

The azo-compound is quite insoluble in mineral acids.

*3-Amino-2-phenylnaphthalene-*1*-azo-β-naphthol*,

$NH_2\cdot C_{10}H_5Ph\cdot N_2\cdot C_{10}H_6\cdot OH$,

can be prepared from the acetyl derivative mentioned above by boiling it with aqueous sodium hydroxide. Two grams were boiled in a Geissler flask with a 15 per cent. solution of sodium hydroxide for two hours, when the solution was filtered and after the insoluble matter had been washed with water it was boiled with concentrated hydrochloric acid and again filtered. A considerable quantity dissolved in the strong acid, forming a deep yellow solution from which on treatment with dilute ammonia the free azo-compound was precipitated as a deep purple solid. When recrystallised from benzene it was obtained in small red plates melting and decomposing at 253°. The compound differs considerably in appearance and melting point from the isomeric 1-amino-2-phenylnaphthalene-3-azo-β-naphthol, and there can be no doubt that the two compounds are different:

0·2101 gave 19·4 c.c. of nitrogen at 19° and 770 mm. N = 10·75.
$C_{26}H_{19}ON_3$ requires N = 10·8 per cent.

*3-Acetylamino-2-phenylnaphthalene-*1 : 4′*-azo-*2′*-phenyl-*1′ : 3′*-naphthylenediamine*, $NHAc\cdot C_{10}H_5Ph\cdot N_2\cdot C_{10}H_4Ph(NH_2)_2$.—This azo-compound is precipitated as the *hydrochloride* when a solution of 0·8 gram of the monoacetyl derivative of 2-phenyl-1 : 3-naphthylenediamine in excess of dilute hydrochloric acid is diazotised by sodium nitrite and added to a solution of 0·7 gram of 2-phenyl-1 : 3-naphthylenediamine also dissolved in dilute hydrochloric acid. The salt crystallises from ethyl alcohol in bright red prisms which decompose at 220°:

0·2035 gave 20·9 c.c. of nitrogen at 13° and 761 mm. N = 12·26.
$C_{34}H_{27}ON_5,HCl$ requires N = 12·5 per cent.

The hydrochloride is practically insoluble in water. The free *azo-compound* is best prepared from the salt by dissolving it in ethyl alcohol, adding sodium hydroxide solution and then precipitating by excess of water. It crystallises from a mixture of benzene and alcohol in small, bright red prisms with slight green reflex which melt at 269° :

0·2059 gave 23·7 c.c. of nitrogen at 15° and 765 mm. N = 13·57.
$C_{34}H_{27}ON_5$ requires N = 13·4 per cent.

3-*Amino-2-phenylnaphthalene*-1 : 4′-*azo*-2′-*phenyl*-1′ : 3′-*naphthylenediamine*, $NH_2\cdot C_{10}H_5Ph\cdot N_2\cdot C_{10}H_4Ph(NH_2)_2$.—In order to prepare this azo-compound from the above acetyl derivative 2 grams were boiled in a Geissler flask with a 15 per cent. aqueous solution of sodium hydroxide for two hours, when the solution was filtered and the insoluble matter after being boiled with dilute hydrochloric acid again filtered. The deep red solution of the dihydrochloride of the azo-compound thus obtained deposited the base as a bright red powder on being made alkaline with ammonia. It was purified by crystallisation from benzene, and obtained in small, deep red prisms with green metallic reflex melting at 231° :

0·1921 gave 24·3 c.c. of nitrogen at 14° and 760 mm. N = 14·88.
$C_{32}H_{25}N_5$ requires N = 14·6 per cent.

The *dihydrochloride*, $C_{32}H_{25}N_5,2HCl$, separates from a solution of the base in strong hydrochloric acid in microscopic red needles. It is readily soluble in hot water containing a trace of hydrochloric acid, forming a deep red solution from which wool is dyed a bright shade of red :

0·2625 gave 0·1340 AgCl. Cl = 12·58.
$C_{32}H_{25}N_5,2HCl$ requires Cl = 12·7.

Combination of Diazonium Salts with the Monoacetyl Derivative of 2-Phenyl-1 : 3-naphthylenediamine.

The combination of the monoacetyl derivative with diazonium salts was investigated in two instances in order to establish the position of the acetyl group. The combination takes place very readily, the azo-group entering in the position (4), that is, in the position adjacent to the acetylamino-group. The compounds formed are therefore true para-azo-compounds and readily form salts with mineral acids, which salts do not differ in colour from the free base. The acetylazo-compounds formed by the acetylation of the corresponding azo-compounds derived from 2-phenyl-1 : 3-naphthylenediamine in combination with diazonium salts (see page 1290) do not form salts with mineral acids.

4-*Benzeneazo-3-acetylamino*-1-*amino-2-phenylnaphthalene*,
$NH_2\cdot C_{10}H_4Ph(NHAc)\cdot N_2Ph$,
separates as a red precipitate on adding a solution of benzenediazonium chloride (made from 0·35 gram of aniline), to which excess of sodium acetate has been added, to a solution of 1 gram of the monoacetyl

derivative dissolved in dilute hydrochloric acid. The azo-compound is very soluble in absolute alcohol, but separates from its concentrated solutions in this solvent as brilliant red needles, without metallic reflex, which melt at 251°:

0·2401 gave 30·3 c.c. of nitrogen at 14° and 759 mm. N = 14·83.
$C_{24}H_{20}ON_4$ requires N = 14·73 per cent.

The azo-compound dissolves in hot concentrated hydrochloric acid, forming a deep red solution from which the *hydrochloride* separates on cooling in microscopic red needles. It is dissociated by water.

4-p-*Nitrobenzeneazo-3-acetylamino-1 amino-2-phenylnaphthalene*,
$NH_2{\cdot}C_{10}H_4Ph(NHAc){\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$,
is formed as a dark red precipitate when a solution of 1 gram of the monoacetyl derivative in dilute hydrochloric acid is mixed with a solution of *p*-nitrobenzenediazonium chloride (prepared from 0·5 gram of *p*-nitroaniline) to which excess of sodium acetate has been added. This precipitate, which consists of the free azo-base, crystallises from a mixture of benzene and alcohol in dark red needles with faint green metallic reflex which melt at 247°:

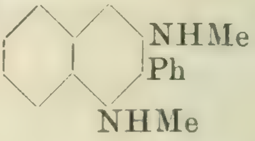
0·1729 gave 23·9 c.c. of nitrogen at 15° and 767 mm. N = 16·35.
$C_{24}H_{19}O_3N_5$ requires N = 16·47 per cent.

The base dissolves in hot concentrated hydrochloric acid, and the deep purple solution thus formed deposits the *hydrochloride* as a deep red crystalline precipitate on cooling. The salt, the solutions of which do not differ appreciably in shade from those of the free base, is dissociated by water.

Both of these acetylazo-compounds on hydrolysis with 15 per cent. aqueous sodium hydroxide yield azo-compounds identical with those derived from the combination of 2-phenyl-1 : 3-naphthylenediamine with benzenediazonium chloride and *p*-nitrobenzenediazonium chloride respectively.

Methylation of 2-Phenyl-1 : 3-naphthylenediamine.

2-Phenyl-1 : 3-naphthylenedimethyldiamine.



As mentioned in the introduction, this base exists in three well-defined forms, two of which are physical isomerides mutually convertible, the one into the other by crystallisation. The third is, however, different, but the relationship between this form and the other two has not as yet been established.

The *dimorphous variety* (*a-form*) is best prepared in the following manner: Twenty grams of 2-phenyl-1 : 3-naphthylenediamine are dissolved in a sufficient quantity of methyl alcohol and 200 grams of methyl sulphate added. The solution is then mixed gradually with a 25 per cent. solution of potassium hydroxide, the contents of the flask being well shaken and cooled after each addition. When the solution, after standing some time, remains strongly alkaline the precipitate which has formed is filtered off and recrystallised from methyl alcohol. The recrystallised product should then be further purified by recrystallising twice from light petroleum (b. p. 90—110°).

The *prisms* are stable at the ordinary temperature and above 80°, and are best obtained by preparing a saturated solution of the base in hot light petroleum (b. p. 90—110°), and allowing crystallisation to take place at 80°. The prisms thus obtained are usually exceptionally large and are always slightly yellow. They melt sharply at 170°.

0·2245 gave 20·7 c.c. of nitrogen at 18° and 759 mm. N = 10·64.

$C_{18}H_{18}N_2$ requires N = 10·7 per cent.

The *needles* are stable between 20° and 80° and can be obtained by preparing a solution of the base in hot light petroleum and then cooling the solution rapidly under running water. The long silky needles thus formed are quite colourless and melt at 164—165°. If the solution containing the needles radiating from the sides of the vessel is left at 17° for twenty-four hours each needle will at the end of this time have been converted into a prism which will be observed adhering to the glass at the point from which the needle radiated. When these prisms are dissolved by warming, the solution again yields the needles on being rapidly cooled :

0·2052 gave 18·1 c.c. of nitrogen at 12° and 769 mm. N = 10·60.

$C_{18}H_{18}N_2$ requires N = 10·7 per cent.

It is worthy of remark that whereas the needles are quite colourless the prisms formed from them are always distinctly yellow and cannot be obtained in a colourless condition even on repeated recrystallisation. This may be entirely due to the difference in the shape and size of the crystals and is probably without other significance.

The *Dihydrochloride*, $C_{18}H_{18}N_2,2HCl$.—Both modifications of the α-form yield the same dihydrochloride, which is best prepared by dissolving either base in hot concentrated hydrochloric acid and allowing the solution to cool. It forms white microscopic needles readily soluble in cold water :

0·2013 gave 0·1695 AgCl. Cl = 20·76.

$C_{18}H_{18}N_2,2HCl$ requires Cl = 20·9 per cent.

The *dinitrosoamine*, $NO\cdot NMe\cdot C_{10}H_5Ph\cdot NMe\cdot NO$, is formed from either modification of the α-form on treatment with nitrous acid, no difference in the behaviour of the two modifications towards this reagent being noticed. In both cases it was observed that the reaction did not proceed very quickly and that several hours had to elapse before it was complete. The compound is precipitated as a pale yellow substance, on adding a slight excess of sodium nitrite solution to a solution of the hydrochloride of the base containing the requisite excess of hydrochloric acid. The precipitation is complete after twelve hours, during which time the solution should be placed in the ice chest. The dinitrosoamine is best purified by recrystallisation from methyl alcohol, from which solvent it separates in small pale yellow needles melting at 174—175°. The compound gives the Liebermann nitroso-reaction :

0·2057 gave 30·4 c.c. of nitrogen at 14·5° and 759 mm. N = 17·40.

$C_{18}H_{16}O_2N_4$ requires N = 17·5 per cent.

The methyl-alcoholic mother liquors from the purification of the dimethyl derivative were evaporated to dryness and the residue, which consisted of a mixture of the dimethyl and trimethyl derivatives, was used subsequently for the preparation of the tetramethyl derivative.

β-Form.—This modification is produced in the following manner: Ten grams of 2-phenyl-1 : 3-naphthylenediamine are added to 65 grams of methyl sulphate, when the base immediately dissolves and a rise in temperature takes place. The solution is warmed at 100° for two hours, after which time the contents of the flask will have become solid owing to the formation of the sulphate of the dimethyl derivative. Water is then added and the excess of dimethyl sulphate decomposed by warming. The clear solution thus obtained, on being rendered alkaline by ammonia, deposits the base as a thick gum which slowly solidifies to a resin on standing. This product was found to consist of two substances, the β-form of the dimethyl derivative which is present to the extent of about 80 per cent. and a trimethyl derivative which is only present in small quantities. These two compounds were separated as follows: The mixed product was rubbed with cold, absolute alcohol, whereby the whole of the trimethyl derivative passed into solution. The residue was then crystallised from hot alcohol, from which solvent the β-form of the dimethyl derivative separated in lustrous colourless plates, the melting point of which was, however, not sharp. The substance was therefore recrystallised twice from alcohol, in the last recrystallisation the alcohol being mixed with a small quantity of benzene, since the pure substance is only sparingly soluble in hot alcohol. It was finally recrystallised from light petroleum (b. p. 90—110°) and obtained in lustrous laminæ melting at 158—159° :

(1) 0·1376 gave 0·4134 CO_2 and 0·0868 H_2O ; C = 81·97 ; H = 7·01
(2) 0·2028 ,, 19·0 c.c. of nitrogen at 24° and 773 mm. N = 10·69.

$C_{18}H_{18}N_2$ requires C = 82·4 ; H = 6·9 ; N = 10·7 per cent.

The *dihydrochloride*, $C_{18}H_{18}N_2,2HCl$, separates as a microcrystalline precipitate on cooling a solution of the base in hot concentrated hydrochloric acid. It dissolves readily in cold water :

0·2173 of the base required 16·4 c.c. of *N*/10 hydrochloric acid.

$C_{18}H_{18}N_2,2HCl$ requires 16·4 c.c.

The *dinitrosoamine*.—The β-form of 2-phenyl-1 : 3-naphthylenedimethyldiamine combines very rapidly with nitrous acid to form the dinitrosoamine and in this respect it differs from the α-form. The dinitrosoamine separates as a pale yellow precipitate on adding the requisite quantity of sodium nitrite solution to a solution of the hydrochloride of the base containing the necessary excess of hydrochloric acid. When purified by recrystallisation from alcohol it is obtained in microscopic buff needles melting at 179°. The compound gives the Liebermann nitroso-reaction.

0·1936 gave 28·8 c.c. of nitrogen at 15·5° and 768 mm. N = 17·62.

$C_{18}H_{16}O_2N_4$ requires N = 17·5 per cent.

The *trimethyl* derivative, $NMe_2 \cdot C_{10}H_5Ph \cdot NHMe$.—The alcoholic mother liquors derived from washing the crude product of methylation already referred to were evaporated to dryness and the residue recrystallised three times from methyl alcohol. The ultimate product consisted of slender, colourless needles, melting at 98—99°, which, from the figures given on analysis and the formation of a mononitrosoamine soluble in acids, evidently possessed a formula corresponding with a trimethyl derivative of 2-phenyl-1 : 3-naphthylenediamine, but whether the dimethylamino-group is in the α- or β-position in the naphthalene ring we were unable to ascertain.

0·2200 gave 19·0 c.c. of nitrogen at 14·5° and 770 mm. N = 10·27.

$C_{19}H_{20}N_2$ requires N = 10·1 per cent.

The *dihydrochloride*, $C_{19}H_{20}N_2,2HCl$, is best formed by titrating the finely-powdered base with *N*/10 hydrochloric acid and evaporating the solution to a small bulk, when the salt crystallises in slender, white needles :

0·1869 of the base required 13·4 c.c. of *N*/10 hydrochloric acid.

$C_{19}H_{20}N_2,2HCl$ requires 13·5 c.c.

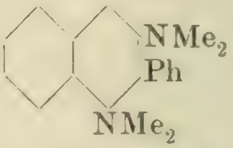
The *nitrosoamine*, $NMe_2 \cdot C_{10}H_5Ph \cdot NMe \cdot NO$, was prepared by dissolving the base in excess of hydrochloric acid, and adding the requisite quantity of sodium nitrite solution. The hydrochloride of the nitrosoamine which remained dissolved was then converted into the free base by means of ammonia and the precipitate recrystallised from alcohol, yielding pale brown needles melting at 151° :

0·1902 gave 21·6 c.c. of nitrogen at 11° and 771 mm. N = 13·71.

$C_{19}H_{19}ON_3$ requires N = 13·8 per cent.

The *hydrochloride*, $C_{19}H_{19}ON_3,HCl$, is best prepared by dissolving the nitrosoamine base in alcohol, adding concentrated hydrochloric acid and allowing the solution to stand. White needles of the salt slowly separate.

*2-Phenyl-*1 : 3-*naphthylenetetramethyldiamine,*



This substance can be produced by the further methylation of the residues from the preparation of the dimethyl derivatives, but was also formed directly from 2-phenyl-1 : 3-naphthylenediamine by the following process:

Ten grams of the base were dissolved in a sufficient quantity of methyl alcohol, mixed with 150 grams of methyl sulphate and then cautiously treated with a 25 per cent. solution of potassium hydroxide until the solution remained strongly alkaline after standing for half an hour. The solid which was then precipitated, after being collected by filtration, was again dissolved in methyl alcohol, mixed with 150 grams of methyl sulphate and again treated with potassium hydroxide solution until permanently alkaline. In order to complete the reaction this process was repeated once more and the ultimate product, after being spread on a porous plate, recrystallised from light petroleum (b. p. 40—50°), when it was obtained in large, colourless prisms melting at 120°:

(1) 0·1624 gave 0·4896 CO_2 and 0·1130 H_2O. C = 82·32 ; H = 7·7.
(2) 0·1684 ,, 14·5 c.c. of nitrogen at 20° and 768 mm. N = 9·8.
$C_{20}H_{22}N_2$ requires C = 82·8. H = 7·6 ; N = 9·6 per cent.

The *dihydrochloride*, $C_{20}H_{22}N_2,2HCl$, separates from solutions of the base in concentrated hydrochloric acid in colourless prisms readily soluble in water:

0·2193 of the base required 15·2 c.c. of *N*/10 hydrochloric acid.
$C_{20}H_{22}N_2,2HCl$ requires 15·1 c.c.

It is worthy of note that, whereas all the other methylated derivatives of 2-phenyl-1 : 3-naphthylenediamine as well as this base itself, form solutions in neutral solvents which exhibit marked violet fluorescence in ordinary daylight, this property is entirely lost in the tetramethyl derivative, the solutions of which do not exhibit fluorescence even when viewed in magnesium light or in the light from the electric arc.

4-*Nitroso-2-phenyl-*1 : 3-*naphthylenetetramethyldiamine,*
$NO{\cdot}C_{10}H_4Ph(NMe_2)_2$.

The tetramethyl derivative is hardly acted on by nitrous acid at 0°, but at 5° is slowly transformed into the above nitroso-derivative. It is best prepared by dissolving the base in excess of hydrochloric acid, adding the theoretical quantity of sodium nitrite solution and allowing the mixture to stand at 5° until no free nitrous acid can be detected. The solution is then made alkaline by means of ammonia, the precipitate collected by filtration and recrystallised from light petroleum (b. p. 90—110°) yielding small, buff-coloured needles, melting at 135°. The compound gives the Liebermann nitroso-reaction :

0·1783 gave 20·3 c.c. of nitrogen at 16° and 752 mm. N = 13·14.

$C_{20}H_{21}ON_3$ requires N = 13·2 per cent.

The Behaviour of the Methylated Derivatives of 2-*Phenyl*-1:3-*naphthylenediamine towards Diazonium Salts.*

The tetramethyl derivative of 2-phenyl-1 : 3-naphthylenediamine is unacted on by diazonium salts, for, although the action of a solution of *p*-nitrobenzenediazonium chloride containing excess of sodium acetate on a solution of the hydrochloride of the base produces a reddish-purple coloration, almost the whole of the tetramethyl derivative used can be recovered unchanged from the solution and it is probable that this coloration, is merely due to the presence of traces of a lower methylated product. The dimethyl derivative reacts partially with benzenediazonium chloride, giving only a small yield of the corresponding azo-compound, but with *p*-nitrobenzenediazonium chloride the interaction is more complete and a 20 per cent. yield of the azo-compound can be obtained under suitable conditions.

4-*Benzeneazo*-2-*phenyl*-1 : 3-*naphthylenedimethyldiamine*,

$(NHMe)_2C_{10}H_4Ph\cdot N_2Ph$,

is formed when a solution of benzenediazonium chloride (from 1 gram of aniline) mixed with a large excess of sodium acetate is added to a solution of 3 grams of the α-form of the dimethyl derivative in dilute hydrochloric acid. The bright red precipitate on being recrystallised twice from alcohol forms small, dark red needles, melting at 139° :

0·1870 gave 24·5 c.c. of nitrogen at 15° and 766 mm. N = 15·47.

$C_{24}H_{22}N_4$ requires N = 15·3 per cent.

The azo-compound dissolves on warming with dilute hydrochloric acid, and the solution on cooling deposits the *hydrochloride* in small, yellow needles. The salt is dissociated by water.

4-p-*Nitrobenzeneazo*-2-*phenyl*-1 : 3-*naphthylenedimethyldiamine*,

$(NHMe)_2C_{10}H_4Ph\cdot N_2\cdot C_6H_4\cdot NO_2$.

This azo-compound is formed when 1·5 grams of the α-form of the dimethyl derivative dissolved in dilute hydrochloric acid are added to a solution of *p*-nitrobenzenediazonium chloride (from 0·9 gram of *p*-nitroaniline) mixed with excess of sodium acetate. A purple substance is precipitated, which, on recrystallisation from benzene containing a little alcohol, yields green needles with strong metallic reflex melting at 180°. The crystals appear green by reflected light, deep purple by transmitted light:

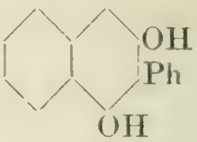
0·2153 gave 31·2 c.c. of nitrogen at 17° and 764 mm. N = 16·91.

$C_{24}H_{21}O_2N_5$ requires N = 17·0 per cent.

The *hydrochloride*.—The azo-compound dissolves in concentrated hydrochloric acid, forming a deep yellow-red solution from which the salt separates on dilution in small, deep yellow needles. It is soluble in hot dilute hydrochloric acid without appreciable dissociation.

The β-form of 2-phenyl-1 : 3-naphthylenedimethyldiamine also reacts with diazonium salts, but we were unfortunately unable to isolate any definite compounds from the products of the interactions.

The Formation of the Corresponding Naphthol and Aminonaphthols from 2-*Phenyl*-1 : 3-*naphthylenediamine.*

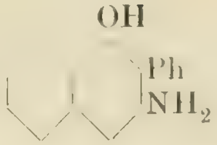
1 : 3-*Dihydroxy-2-phenylnaphthalene*,  .

This substance has been prepared by Volhard (*Annalen*, 1897, **296**, 16) by the action of concentrated sulphuric acid on ethyl diphenylacetoacetate. It can be prepared from 2-phenyl-1 : 3-naphthylenediamine with a yield of 80 per cent. by the following process: Five grams of the diamino-base were dissolved in excess of a 10 per cent. hydrochloric acid, and the solution heated in a Carius tube at 180° for eighteen hours. The liquid in the tubes on cooling were colourless, and a black tarry bead lay at the bottom. The mother liquor was poured off, the tarry matter dissolved in dilute sodium hydroxide, and the solution quickly filtered. Owing to the rapid oxidation of the alkaline solution, it was necessary during this process to pass a current of carbon dioxide over the liquid in order, as far as possible, to exclude air. The solution on acidifying deposited the dinaphthol which was purified by recrystallisation from dilute alcohol and obtained in almost colourless plates melting at 165°:

0·1441 gave 0·4270 CO_2 and 0·0720 H_2O. C = 80·91; H = 5·38.

$C_{16}H_{12}O_2$ requires C = 81·3; H = 5·1 per cent.

The properties of this compound have been fully described by Volhard.

3-Amino-1-hydroxy-2-phenylnaphthalene, 

The acetyl derivative of this aminonaphthol, namely, *3-acetylamino-1-hydroxy-2-phenylnaphthalene*, $NHAc\cdot C_{10}H_5Ph\cdot OH$, can be readily prepared by boiling the diazonium salt of the monoacetyl derivative of 2-phenyl-1 : 3-naphthylenediamine (see page 1293) with water, and for this purpose the following process was found most convenient: Three grams of the monoacetyl derivative were dissolved in excess of dilute sulphuric acid and the solution diazotised at 0° with a solution of sodium nitrite. When a slight excess of nitrous acid was indicated by potassium iodide and starch paper, the clear diazo-solution was warmed on the water-bath until nitrogen ceased to be evolved, then cooled and filtered. The insoluble precipitate was then treated with potassium hydroxide solution, when it practically all dissolved, and the solution on acidifying deposited the acetyl derivative of the aminonaphthol as a pale yellow solid which on recrystallisation from a mixture of benzene and alcohol was obtained in almost colourless plates melting at 203° :

0·2128 gave 9·4 c.c. of nitrogen at 14° and 763 mm. N = 5·24.
$C_{18}H_{15}O_2N$ requires N = 5·1 per cent.

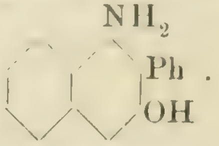
The acetyl derivative is readily soluble in dilute caustic alkalis, and the solution does not oxidise on exposure to the air.

The free aminonaphthol was prepared from the acetyl derivative by boiling it with a 20 per cent. solution of potassium hydroxide for three hours. After being heated for the requisite time the solution was filtered and the aminonaphthol precipitated by dilute hydrochloric acid. It was purified by recrystallisation from a mixture of benzene and alcohol, being obtained in small needles melting at 185° :

0·1824 gave 9·5 c.c. of nitrogen at 16° and 757 mm. N = 6·05.
$C_{16}H_{13}ON$ requires N = 6·0 per cent.

3-Amino-1-hydroxy-2-phenylnaphthalene is readily soluble in alkalis and its solutions in this reagent become rapidly coloured red on shaking with air. It forms salts with acids which are stable in strongly acid solutions, but which are dissociated by water.

1-Amino-3-hydroxy-2-phenylnaphthalene,



This aminonaphthol is formed when the monohydrochloride of 2-phenyl-1 : 3-naphthylenediamine is heated in a sealed tube at 140° for eighteen hours. Before preparing this substance, however, the method of formation of the monohydrochloride was determined. When 2-phenyl-1 : 3-naphthylenediamine is titrated with $N/10$-hydrochloric acid, the base is found to take up an amount of acid corresponding with the formation of a dihydrochloride. If, however, an amount of hydrochloric acid necessary to form the monohydrochloride is added, the base passes into solution, and on evaporating to dryness in an evacuated desiccator over potash, the *monohydrochloride* $C_{16}H_{14}N_2,HCl$, is obtained in slender, colourless needles:

0·2175 gave 0·1139 AgCl. Cl = 12·91.

$C_{16}H_{14}N_2,HCl$ requires Cl = 13·0 per cent.

The salt is readily soluble in water, and after the aqueous solution has been heated in a sealed tube, the product on cooling is found to consist of the above aminonaphthol, which can be purified by repeated recrystallisation from benzene and obtained in colourless plates melting at 208°:

0·2021 gave 10·9 c.c. of nitrogen at 20° and 757 mm. N = 6·18.

$C_{16}H_{13}ON$ requires N = 6·0 per cent.

The aminonaphthol appears to be much more readily oxidised in the air than the 3 : 1-derivative, and can only be obtained in a colourless form by repeated recrystallisation. Like its isomeride, it is readily soluble in caustic alkalis, and forms salts with strong mineral acids which are dissociated by water.

The further investigation of the properties of these aminonaphthols, as well as of the isomeric dimethyl derivatives of the diamino-base, is in progress.

The authors desire to express their indebtedness to the Badische Anilin- und Soda-Fabrik for kindly placing at their disposal a large quantity of phenylacetonitrile for the purposes of this research.

MANCHESTER UNIVERSITY.

CXX.—*New Derivatives of Diphenol (4′ : 4′ Dihydroxydiphenyl).*

By JAMES MOIR, D.Sc., M.A.

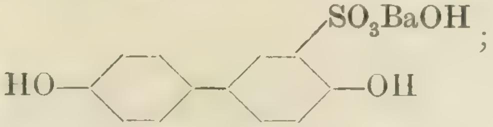
THE diphenol used in the present investigation was prepared from benzidine by the diazo-reaction. By distillation and crystallisation from alcohol it was obtained in aggregates of short, white needles melting at 274° (uncorr.).

Diphenol is readily soluble in alcohol, acetone, or boiling acetic acid. When neutral ferric chloride is added to its aqueous solution, a brown precipitate of diphenoquinhydrone is produced, and a violet precipitate of the alkali salt of the latter is obtained on adding a solution of iodine to a solution of diphenol in the least possible quantity of strong caustic soda (compare Willstätter and Kalb, *Ber.*, 1905, **38**, 1232; Moir, Proc., 1906, **22**, 110).

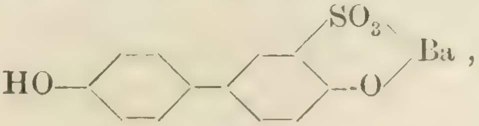
Diphenol dibenzoate has not hitherto been described; when prepared by the Schotten-Baumann method, it forms opaque, white needles, nearly insoluble in all solvents except boiling glacial acetic acid, which melt at 241°. It is insoluble in caustic alkali and is only slowly hydrolysed by it on heating.

Sulphonation of Diphenol.

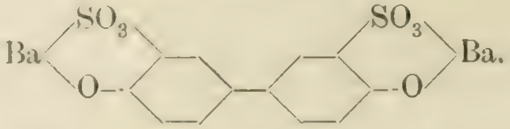
On sulphonating diphenol with ordinary sulphuric acid at temperatures below 100°, the 3 : 3′-*disulphonic acid* is the sole product. At 120° a quantity of the 3 : 5 : 3′-*trisulphonic acid* is also formed and at 180° the 3 : 5 : 3′ : 5′-*tetrasulphonic acid* is the sole product. All the salts of the latter are very soluble in water, thus differing from those described by Griess. The author considers that Griess' substances are really basic salts of diphenolmonosulphonic and diphenoldisulphonic acids; which indeed follows from their mode of preparation; he suggests that the substance to which Griess gave the formula $(C_{12}H_7O_{11}S_3)_2Ba_3$ is to be represented by the formula



the substance $C_{12}H_6O_{14}S_4Ba_2$ by the formula



and the substance $C_{12}H_6O_{15}S_4Ba_3$ by the formula



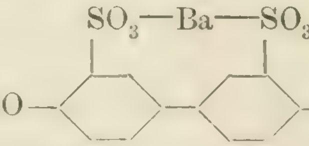
All the existing analyses of these compounds agree quite well with these suppositions. On boiling the sulphonic acids prepared by the author with nitric acid, they are converted quantitatively into Kunze's tetranitrodiphenol, melting at 225° (*Ber.*, 1888, **21**, 3331 and 3531).

Sodium 4 : 4′-*diphenol*-3 : 3′-*disulphonate.*—To prepare this acid the powdered diphenol is added to ordinary sulphuric acid and the mixture heated on the water-bath so long as the phenol continues to dissolve; the sulphonic acid sometimes separates out. If the diluted solution is made alkaline with sodium hydroxide, after a time a slimy, microcrystalline precipitate of the *sodium* salt is obtained, which may be separated on a porous tile and purified by recrystallisation. It forms very small needles, somewhat easily soluble in water:

0·3310 (air-dried) gave 0·1136 Na_2SO_4. Na = 11·13.
$C_{12}H_{10}O_8S_2Na_2,H_2O$ requires Na = 11·29 per cent.

On adding barium hydroxide to its solution, an insoluble, basic barium salt is precipitated. If this be separated and boiled with dilute acetic acid, a solution is obtained from which the normal *barium* salt crystallises on cooling in long, opaque, pearly needles, rather sparingly soluble in water:

0·4928 (dried in a vacuum) gave 0·0353 H_2O (170°) and 0·2193 $BaSO_4$. H_2O = 7·16; Ba = 26·19.
0·2172 (dried at 120°) gave 0·0993 $BaSO_4$. Ba = 26·90.

The formula, HO  OH + $2H_2O$ requires H_2O = 6·96. Ba = 26·55 per cent.

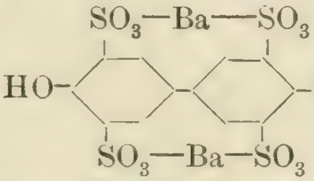
The salt appears to be identical with that described by Limpricht (*Annalen*, 1891, **261**, 334).

The *potassium* salt forms small, sparingly soluble needles. *Potassium*-4 : 4′-*diphenol*-3 : 5 : 3′-*trisulphonate* is obtained when diphenol is digested at 100—120° during an hour with ten times its weight of sulphuric acid. The diluted solution is neutralised with barium hydroxide until a flocculent precipitate of the basic salt begins to appear, then filtered, and neutralised with potassium carbonate. The potassium salt is precipitated by alcohol and purified by recrystallisation from hot water. It forms small, shiny, rectangular anhydrous plates:

0·2969 (dried at 100°) gave 0·1444 K_2SO_4. K = 21·80.
$C_{12}H_9O_{11}S_8K_3$ requires K = 21·67 per cent.

Sodium 4 : 4′-*diphenol*-3 : 5 : 3′ : 5′-*tetrasulphonate.*—This is the most easily prepared sulphonic acid of diphenol. To obtain it, diphenol is heated with excess of sulphuric acid during half an hour at 160—170°. The liquid is at first very dark blue, but soon becomes paler, a little sulphur dioxide being evolved. The solution is treated with saturated brine and then neutralised with sodium carbonate, when the *sodium* salt separates in microscopic needles easily soluble in water. When dried it turns blue owing to superficial oxidation, which also occurs on exposure to nitrous fumes :

0·1330 (dried at 100°) gave 0·0625 Na_2SO_4. Na = 15·22.
$C_{12}H_6O_{14}S_4Na_4$ requires Na = 15·48 per cent.

The *barium* salt, , is obtained by neutralising the sulphonation mixture with excess of barium carbonate, treating the filtrate with a little barium acetate, and concentrating; it forms anhydrous, opaque, white needles, very soluble in water :

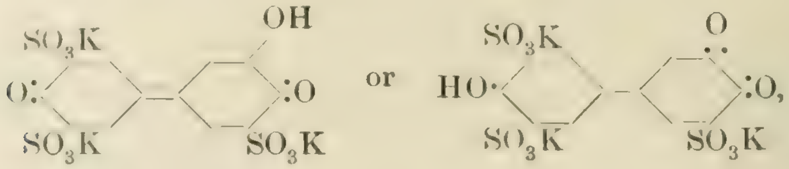
0·5895 (dried at 90°) gave 0·3526 $BaSO_4$. Ba = 35·20.
$C_{12}H_6O_{14}S_4Ba_2$ requires Ba = 35·36 per cent.

The potassium salt is very soluble, and has not been obtained in a condition suitable for analysis. The free sulphonic acid is also extremely soluble in water.

On treating the original sulphonation mixture with ferric chloride, a dark violet coloration is produced, which does not fade on exposure to sunlight, but is bleached to a yellow shade by strong acids or alkalis. Other oxidising agents produce only a pale yellow colour. The spectrum is continuous. An attempt was made to isolate the substance in the solid state by mixing solutions of the barium salt of the tetrasulphonic acid and ferric sulphate, and concentrating the violet filtrate on the water-bath. Indistinct, indigo-coloured crystals were obtained, which, however, altered on drying to an olive-green solid, the latter when redissolved giving also a green solution. On treatment with potassium carbonate and separating the ferric hydroxide, a deep orange solution (free from iron) was obtained, which on evaporation gave dark red crystals of a basic potassium salt, too soluble to investigate. On adding acetic acid to its warm solution, bright scarlet crystals were obtained, which were recrystallised for analysis :

0·4404 (dried at 90°) gave 0·1997 K_2SO_4. K = 20·37.

This cannot be the diphenoquinonetetrasulphonate, which requires K = 23·8 per cent. Its constitution is probably expressed by one of the following (tautomeric) formulæ:



which require K = 21·17 per cent.

This constitution is confirmed by the fact that, when reduced by zinc dust and acid (it resists sulphites or sulphur dioxide), the colourless solution gives the olive-green coloration with ferric chloride characteristic of adjacent dihydroxybenzenes. Although it has been suggested (Proc., 1906, **22**, 111) that the original violet substance (which closely resembles Kunze's "tetra-aminodiphenoquinone," *Ber.*, 1888, **21**, 3331 and 3531) is a derivative of "diphenoquinhydrone," nevertheless it gives only a faint coloration with concentrated sulphuric acid, and thus seems not to be analogous to cœrulignone; still, it is possible that this fact is due to its acidic character inhibiting the formation of an oxonium salt.

Potassium 5 : 5′-*Dibromo* - 4 : 4′-*diphenol* - 3 : 3′-*disulphonate.*—Ten grams of the potassium trisulphonate, in warm water, were treated with 1 c.c. of bromine. The whole solidified to an olive-green jelly, which, on warming, faded in colour and dissolved. On filtering and cooling, the product was obtained in fine rosettes of needles, which were recrystallised for analysis. A further quantity was obtained from the filtrate by adding alcohol:

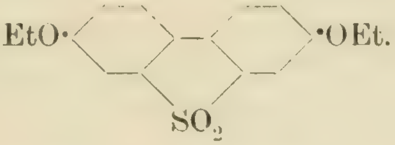
0·3043 (dried at 130°) gave 0·0851 K_2SO_4. K = 12·54.
0·2372 ,, ,, 0·1528 AgBr. Br = 27·40.
$C_{12}H_6O_8Br_2S_2K_2$ requires K = 13·45; Br = 27·58 per cent.

On adding ferric chloride to its solution, an inky colour and precipitate are obtained, the latter being soluble in hot water.

Sulphonation of Diphenetole.

Diphenetole, suspended in carbon disulphide, was very gradually mixed (through the condenser) with an equal weight of chlorosulphonic acid. After removing the solvent, the dark blue product was repeatedly extracted with boiling water. The insoluble, green residue was then crystallised from excess of boiling glacial acetic acid, from which it separated in long, white needles melting at 208°.

These were found to contain a little chlorine, not removable by boiling aqueous sodium hydroxide. The chlorine is most probably adventitious, and the substance, judging from its properties, must be *diphenetolesulphone*,



On analysis :

0·1844 gave 0·1528 $BaSO_4$. S = 11·38.

$C_{16}H_{16}O_4S$ requires S = 10·53 per cent.

On rendering the aqueous extract alkaline with potassium carbonate, a microcrystalline precipitate of the mixed sulphonates was formed. Fractional crystallisation gave (1) very sparingly soluble, extremely small needles of the *monosulphonate* :

0·6455 (dried at 120°) gave 0·1704 K_2SO_4. K = 11·82.

$C_{16}H_{17}O_5SK$ requires K = 10·86 per cent.,

and (2) soapy, lustrous plates, with pronounced bitter taste, rather easily soluble in water, of the *disulphonate* :

0·5306 (dried at 125°) gave 0·1902 K_2SO_4. K = 16·09.

$C_{16}H_{16}O_8S_2K_2$ requires K = 16·32 per cent.

Nitration of Diphenol.

On nitrating diphenol, in addition to Kunze's tetranitrodiphenol (*loc. cit.*) and Schütz's dinitrodiphenol, melting at 272° (*Ber.*, 1888, **21**, 3531), another nitro-compound was obtained which apparently is identical with the dinitrodiphenol prepared by Goldstein (*J. Russ. Phys. Chem. Soc.*, 1874, **6**, 193). As it is probable from Goldstein's method of preparing this substance that it is a 3 : 3′-dinitrodiphenol, it is to be supposed that Schütz's dinitrodiphenol is differently constituted.

On adding two equivalents of strong nitric acid to a solution of diphenol in acetic acid at 50°, the chief product was Kunze's dinitrocompound, which forms dark chestnut needles melting at 272°. A small quantity of a nearly black substance, which does not melt and is insoluble in all solvents, was also observed. On diluting the mother liquor from Kunze's compound, yellow warts, melting at about 181°, were obtained. This was first purified by dissolving in sodium hydroxide and adding an excess of the latter, when the maroon sodium salt separated. It possesses a bronze-green lustre. It was dissolved in water and precipitated with barium chloride as a brick-red, basic barium salt, which, on acidifying, gave the free dinitrodiphenol. On recrystallisation this formed minute, sulphur-yellow rhombs melting at 191°.

Goldstein's experiment (oxidation of *o*-nitrophenol) was also repeated. The product is a mixture (a derivative of 2 : 2′-diphenol being present) ;

the sparingly soluble substance melted at 185—190°, and behaved just like the above in all particulars examined, but the question of their identity remains to be determined.

Tetranitrodiphenol was obtained as sole product by dissolving diphenol in sulphuric acid at 100°, cooling, diluting, and heating with excess of nitric acid until separation of the yellow solid was complete. The crude product melted at 221°; after crystallisation from absolute alcohol, it formed golden-yellow needles melting at 225°.

5 : 5′-*Dibromodinitrodiphenol* (?).—Schütz's dinitrodiphenol was dissolved in aqueous sodium hydroxide, reprecipitated in a state of fine division by acid, and then mixed with excess of bromine dissolved in acetic acid.

A chocolate-coloured perbromide was formed, and the mixture was boiled for some time until free from bromine. The precipitate was collected, boiled with sodium sulphite, and acidified, when the new substance was obtained as a yellow precipitate, which turned chestnut-brown on exposure. When recrystallised from acetone mixed with water, it melted at 237°. The analyses were unsatisfactory, being 2 to 3 per cent. below that required by the formula $C_{12}H_6O_2Br_2(NO_2)_2$, which requires Br = 36·85 per cent.

3′-*Bromo-3-nitrodiphenol.*—Diphenol was dissolved in hot sulphuric acid, diluted, and treated with bromine; the solution was boiled and nitric acid added gradually to it until the separation of the bromonitrodiphenol was complete. On fractional crystallisation, the new compound separated in small, golden prisms melting at 219°:

0·2682 gave 0·1670 AgBr. Br = 26·50.

$C_{12}H_8O_4NBr$ requires Br = 25·80 per cent.

5 : 5′-*Dibromo*-o-*tolidine.*—This was obtained by brominating tolidine in acid solution. A blue, quinhydronic, intermediate compound is formed in the cold, and is only converted with some difficulty into the dibromotolidine, which crystallises from alcohol in white needles melting at 195°.

On diazotising it (which is effected only with great difficulty), the solution was found to be unaltered by boiling. When boiled with 20 per cent. sodium hydrogen sulphate solution the product was insoluble in alkali and dark brown, like the substance obtained by Cain from dianisidine (Trans., 1903, **83**, 688).

5 : 5′-*Dibromo*-o-*dicresol* was prepared from *o*-dicresol by brominating it in cold acetic acid solution. After boiling the mixture with bisulphite solution, the dibromodicresol separated in white needles melting at 185°:

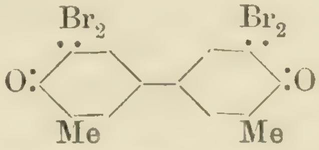
0·2258 gave 0·2283 AgBr. Br = 43·03.

$C_{14}H_{12}O_2Br_2$ requires Br = 43·00 per cent.

Under certain obscure conditions, another white, brominated substance, melting at 163°, is occasionally formed.

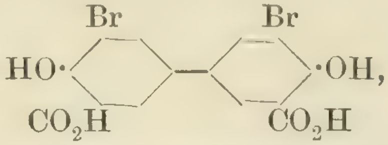
Dibromodicresol Perbromide.—On adding excess of bromine to an acetic acid solution of the above substance, an olive-green, quinhydronic substance was precipitated. On boiling, the whole dissolved to a deep red solution. This was poured into water, giving a bright scarlet precipitate, which was washed with water and dilute alcohol, and dried in a vacuum. It melts at about 96°, evolving hydrogen bromide, and is insoluble in alkali.

From analogy to tribromophenol bromide it appears probable that this compound may have the constitution:



0·1927 (dried at 60°) gave 0·2746 AgBr. Br = 60·65.

$C_{14}H_{10}O_2Br_4$ requires Br = 60·36 per cent.

Dibromodisalicylic acid, presumably  has

been obtained from dianthranilic acid, either by diazotising and then brominating or vice versa. It forms brown needles melting above 300°, and is soluble in alkali carbonates, but is nearly insoluble in all organic solvents.

The author wishes to state that practically the whole of this work was done at the Central Technical College, South Kensington, in 1902, but has remained unpublished for lack of analytical data.

Chemical Laboratory,
Mines Department,
Transvaal.

CXXI.—*A Series of Coloured Diazo-salts Derived from Benzoyl*-1 : 4-*naphthylenediamine.*

By Gilbert T. Morgan and William Ord Wootton.

In this communication the authors give the results of a further study of the diazo-derivatives of the monoacylated para-diamines, their experiments being devised with the view of ascertaining the joint influence of the acyl group and the aromatic nucleus on the nature of the products of diazotisation.

It had already been ascertained that benzoyl-*p*-phenylenediamine furnished a series of stable diazonium salts including both a carbonate and a nitrite (Trans., 1905, 87, 933), but as the cyanides of this series had not been isolated satisfactorily the investigation was extended to benzoyl-1 : 4-naphthylenediamine, with the result that a very complete series of stable diazo-derivatives, including a well-defined cyanide, has been obtained, and the noteworthy fact discovered that all these compounds are distinctly coloured.

The diazotisation of benzoyl-1 : 4-naphthylenediamine hydrochloride leads to the production of a yellow, crystalline diazonium chloride which is so stable that it can be crystallised from hot water or boiling alcohol. The other diazonium salts of this series were usually made by double decomposition, as they are only sparingly soluble in water. The bromide, sulphate, nitrate, chlorate, thiocyanate, nitrite, carbonate and other salts described in the experimental section of the paper are all yellow, crystalline compounds. The perchlorate is the most insoluble and least coloured salt of the series; it separates from very dilute aqueous solutions as a pale yellow, crystalline precipitate, and is quite stable in the dry state.

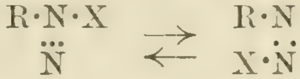
These salts retain their colour when exposed to the temperature of liquid air, and when soluble in water their solution is distinctly yellow. They couple readily with alkaline *β*-naphthol and show the other properties of diazonium salts. The aqueous solution of the diazonium chloride is neutral to litmus, and when treated with a small proportion of alkali or even sodium acetate, a yellowish-brown nitrosoamine, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}NH{\cdot}NO$, is precipitated. With excess of aqueous caustic alkali this substance gives an alkali derivative which, like the nitrosoamine itself, does not couple with alkaline *β*-naphthol. This property is, however, regained when the nitrosoamine is dissolved in mineral acids, the corresponding diazonium salt being formed.

When the foregoing diazonium salts are treated with alcoholic potash, the nitrosoamine produced at first dissolves to form the soluble potassium derivative, which then undergoes reduction in accordance with the following equation:

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}OK + C_2H_6O = C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7 + N_2 + C_2H_4O + KOH.$$

When alcoholic solutions of these diazonium salts are treated with aqueous potassium cyanide, a stable, red cyanide is immediately produced which, unlike the diazonium salts, does not couple with alkaline *β*-naphthol. The red cyanide, when allowed to remain for about twenty hours in alcoholic solution containing a trace of potassium cyanide, becomes transformed into a more soluble, yellow modification, which is precipitated on the addition of water. This substance also is incapable of coupling with alkaline β-naphthol. Both cyanides dissolve in cold concentrated sulphuric acid, giving red solutions which rapidly assume a yellow tint. If at this stage the liquid is diluted with water and poured into alkaline β-naphthol, the azo-condensation occurs.

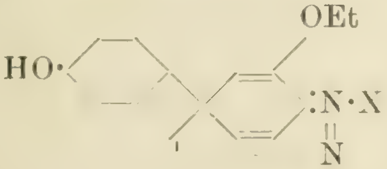
The existence of coloured diazo-salts has already been indicated by Hantzsch (*Ber.*, 1900, **33**, 2183, and 1901, **34**, 4168) in a comparative study of the chlorides, bromides, iodides, and thiocyanates of the simpler diazonium bases. He found that whereas the chlorides and bromides were almost invariably colourless, yet the iodides and thiocyanates were generally coloured and also very unstable. On this account, Hantzsch assumed that these coloured unstable products were equilibrium mixtures of diazonium and *syn*-diazo-compounds.



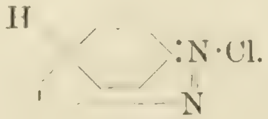
$$\begin{array}{c}R\cdot N\cdot X\\ \vdots\\ N\end{array} \rightleftarrows \begin{array}{c}R\cdot N\\ \cdot\,\cdot\\ X\cdot N\end{array}$$

This equilibrium can be modified in the sense of increasing the proportion of diazonium salt either by dissolving the substance in water, when a colourless solution is obtained, or by cooling the solid considerably, when it undergoes an appreciable loss in colour.

More recently, Cain (Trans., 1905, **87**, 5) has obtained from 4′-hydroxy-3-ethoxydiphenyldiazonium hydroxide a series of coloured salts possessed of considerable stability, to which in accordance with this author's views (this vol., p. 1040) the formula (I) should be ascribed:



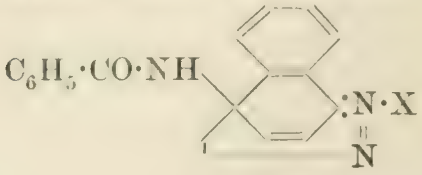
(I.)



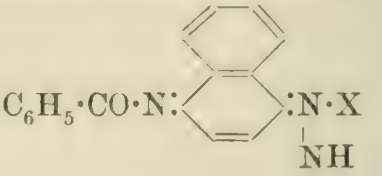
(II.)

It is manifest that the unstable coloured diazo-compounds obtained by Hantzsch differ considerably from those prepared by Cain and by the authors. In the former series the acid ion is the factor which apparently determines the colour, for with the same diazonium ion Hantzsch found that the chloride and bromide were colourless, whereas the iodide and thiocyanate were coloured. In the latter series described by Cain and the authors, the nature of the acid ion is certainly not the determining factor, for all the diazonium salts of this group are more or less coloured. Moreover, the appearance of colour is associated with an increase rather than a decrease in stability.

The assumption that these stable coloured diazo-salts are wholly or in part *syn*-diazo-derivatives is not justifiable from the experimental evidence available at present. The behaviour of these coloured diazonium salts derived from benzoyl-1 : 4-naphthylenediamine is in accord with Cain's formulation, and accordingly the series may be represented by the formula (III), in which these salts are given the same configuration as the colourless benzenediazonium chloride (II) :



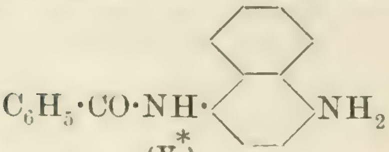
(III.)



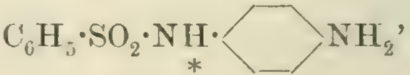
(IV.)

The formula advocated by Cain is applicable both to the simpler colourless diazonium salts and also to the more complex coloured diazo-derivatives described in this communication, the development of colour in the latter series being attributed by the authors to the presence of a complex radicle in the para-position with respect to the diazo-nitrogen and to the substitution of a naphthalene for a benzene nucleus.*

The alternative configuration, (IV), for the 4-benzoylaminonaphthalene-1-diazonium salts has been suggested by Hewitt (Proc., 1907, **23**, 181), according to which a base yielding coloured diazonium salts should contain a labile hydrogen atom * (V) which migrates to the diazo-nitrogen during the process of diazotisation.



(V.)



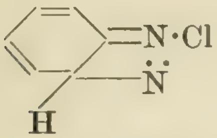
(VI.)

It still, however, remains to be demonstrated that this migration of hydrogen is necessary for the development of colour among diazonium salts, and experiments bearing on this point are in progress. The converse statement that a coloured diazonium salt will result when a labile hydrogen atom is present, is certainly not generally true, for benzenesulphonyl-*p*-phenylenediamine (VI) yields colourless diazonium salts (chloride, sulphate, etc.) although it contains a very labile hydrogen atom (Morgan and Micklethwait, Trans., 1905, **87**, 81).

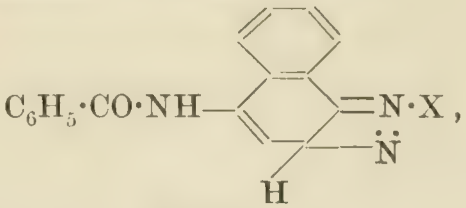
In connexion with the hypothesis of a quinonoid structure for diazonium salts, it should be remembered that Griess originally held the view that two carbon atoms of the nucleus are in some way involved in the diazonium complex, or, in other words, that benzenediazonium nitrate, "$C_6H_4N_2,HNO_3$," and sulphate, "$C_6H_4N_2,H_2SO_4$," are disubstituted derivatives of benzene (*Annalen*, 1866, **137**, 47). Now inasmuch as both benzene and naphthalene nuclei can assume an ortho-quinonoid configuration, the possibility that their diazo-derivatives may have a similar structure must be taken into account. This view is expressed by the following formulæ (VII) and (VIII):

---

* The influence of the naphthalene nucleus in intensifying the colour of diazonium salts is exemplified by the diazonium chlorides derived from α- and β-naphthylamines which are described respectively as orange and yellow compounds (Knoevenagel, *Ber.*, 1895, **38**, 2057).



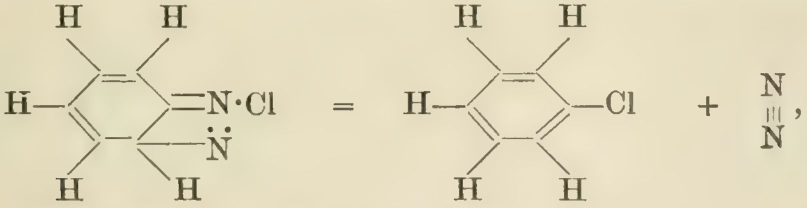
(VII.)



(VIII.)

in which the former represents the colourless benzenediazonium chloride, whilst the latter indicates the alternative ortho-quinonoid configuration for the coloured diazonium salts described in this communication.

In these two formulæ the diazo-nitrogens are represented as being attached to the ortho-quinonoid nucleus forming an unstable four-membered ring and hence readily detachable, as in the Sandmeyer reaction:



with the regeneration of a benzenoid nucleus.

A comparative study of the colourless and coloured diazonium salts is in progress, the object of the investigation being to arrive at some decision with regard to the several alternative quinonoid formulæ now proposed for this group of substances.

EXPERIMENTAL.

*Diazo-derivatives of Benzoyl-*p*-phenylenediamine.*

p-Aminobenzanilide hydrochloride, obtained by saturating a benzene solution of the recrystallised base with hydrogen chloride, was made into a thin paste with glacial acetic acid, and treated with amyl nitrite diluted with its own volume of the same solvent. Benzoyl-*p*-aminobenzenediazonium chloride was thus precipitated in the form of a pale brown, granular powder.

*Benzoyl-*p*-aminobenzenediazonium thiocyanate,*

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}CNS,$$

was prepared by adding an excess of aqueous potassium thiocyanate to the clear solution produced by mixing the sparingly soluble diazonium chloride with a saturated solution of sodium acetate. An almost white, amorphous precipitate was formed which gradually assumed a yellowish-brown tint, and separated into a bulky mass of long, filamentous needles. When recrystallised from alcohol, the compound separated in long, lustrous brown needles often one centimetre in length:

0·2081 gave 0·1807 $BaSO_4$. $S = 11·91$.

$C_{14}H_{10}ON_4S$ requires $S = 11·34$ per cent.

This thiocyanate gave a scarlet coloration with alkaline β-naphthol, and hence may be regarded as a diazonium salt.

Benzoyl-p-*aminobenzenediazonium picrate*,

$$C_6H_5·CO·NH·C_6H_4·N_2·O·C_6H_2(NO_2)_3,$$

separated as a pale yellow precipitate on mixing a warm saturated solution of picric acid in 30 per cent. alcohol with an aqueous solution of the foregoing diazonium chloride. The yield is almost theoretical, and the product when crystallised from warm alcohol forms rosettes of yellow needles melting and decomposing at 132°:

0·2119 gave 31·2 c.c. nitrogen at 17° and 770 mm. $N = 17·60$.

$C_{19}H_{12}O_8N_6$ requires $N = 18·58$ per cent.

A similar compound, *acetyl*-p-*aminobenzenediazonium picrate*, obtained from *p*-aminoacetanilide, crystallised from boiling alcohol in glistening, yellow needles. As these picrates may be precipitated from solutions of the diazonium chloride even in the presence of excess of mineral acid, and as they couple readily with alkaline β-naphthol, they must be regarded as diazonium salts.

Diazo-derivatives of Benzoyl-1 : 4-*naphthylenediamine.*

Benzo-α-naphthalide was nitrated according to the method given by Worms (*Ber.*, 1882, **15**, 1813), and the product when dissolved in hot glacial acetic acid yielded, on cooling, benzoyl-4-nitro-α-naphthylamine, whilst the isomeride, benzoyl-2-nitro-α-naphthylamine, was recovered from the mother liquors by diluting these with three volumes of water.

Benzoyl-1 : 4-naphthylenediamine was obtained by suspending 100 grams of the foregoing *p*-nitro-compound in 900 c.c. of boiling alcohol, and adding gradually 300 c.c. of concentrated hydrochloric acid, and 70 grams of tinfoil. The nitro-compound dissolved completely in about two hours, and benzoyl-1 : 4-naphthylenediamine hydrochloride separated on cooling as a flocculent precipitate, which was crystallised from water acidified with hydrochloric acid. The base, set free with sodium carbonate, was crystallised from alcohol, when it was obtained in colourless needles melting at 187° (compare Hübner, *Annalen*, 1881, **208**, 326).

Benzoylbenzylidene-1 : 4-*naphthylenediamine*,

$$C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N{:}CH\cdot C_6H_5,$$

produced on warming together in alcoholic solution equivalent quantities of benzoyl-1 : 4-naphthylenediamine and benzaldehyde, was recrystallised from alcohol and glacial acetic acid; it separated in yellow needles, and melted at 196—197°.

4-*Benzoylaminonaphthalene*-1-*diazonium chloride*,

$$C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot Cl.$$

—Benzoyl-1 : 4-naphthylenediamine hydrochloride is not readily diazotised with hydrochloric acid and sodium nitrite, and the following treatment was found to give the best result. Ten grams of the base dissolved in the least possible amount of a mixture of one part of glacial acetic acid and four parts of alcohol were treated with 16 c.c. of concentrated hydrochloric acid mixed with 32 c.c. of hot alcohol, when the mixture immediately set to a stiff paste. When the temperature of the mass had fallen to 40°, 20 c.c. of amyl nitrite were added in four lots of 5 c.c. each. The paste became reddish-yellow, and when kept for 10—15 minutes at 50° it changed to a clear liquid which was filtered from a slight impurity; the filtrate was warmed again and treated with several volumes of warm ether. The diazonium chloride rapidly separated in warty aggregates of straw-coloured needles, the yield being almost quantitative:

0·069 gave 0·0324 AgCl. Cl = 11·61.
0·1320 ,, 15·6 c.c. nitrogen at 21° and 766 mm. N = 13·54.
$C_{17}H_{12}ON_3Cl$ requires Cl = 11·47, N = 13·57 per cent.

The diazonium chloride may be recrystallised either from hot water or from warm alcohol and ether, when it separates in glistening, yellow needles which are stable on exposure to light. It melts and decomposes at 140—143°. The yellow colour is retained even after repeated crystallisations, the palest specimens being obtained by fractionally precipitating its alcoholic solution with ether. The aqueous solution of this chloride is neutral to litmus paper, and this, together with the fact that the compound readily couples with alkaline β-naphthol to form an azo-derivative (compare p. 1322), supports the view that the substance must be regarded as a true diazonium salt.

The diazonium chloride also condenses with aniline to form an unstable, yellow diazoamine, which rapidly changes to a red azo-derivative.

4-*Benzoylaminonaphthalene*-1-*diazonium bromide*,

$$C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot Br,$$

separates in yellow needles on mixing aqueous solutions of potassium bromide and the diazonium chloride; it is non-explosive and melts at

148—149°. Its colour is intermediate between that of the chloride and iodide:

0·2064 gave 0·1124 AgBr. Br = 23·15.

$C_{17}H_{12}ON_3Br$ requires Br = 22·67 per cent.

4-*Benzoylaminonaphthalene*-1-*diazonium iodide*,

$C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot I$,

which is precipitated in small, orange-coloured prisms on mixing aqueous solutions of potassium iodide and the diazonium chloride, is very sparingly soluble in water, and melts at 97—98°.

4-*Benzoylaminonaphthalene*-1-*diazonium platinichloride*,

$(C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2)_2PtCl_6$,

is a dark yellow, microcrystalline powder, sparingly soluble in alcohol or water, obtained by adding excess of platinic chloride to an alcoholic solution of the diazonium chloride:

0·1751 gave 0·0363 Pt. Pt = 20·73.

$C_{34}H_{24}O_2N_6Cl_6Pt$ requires Pt = 20·39 per cent.

When suspended in alcohol and exposed to light, this compound undergoes decomposition.

4-*Benzoylaminonaphthalene*-1-*diazonium sulphate*,

$C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot HSO_4$.

—Amyl nitrite (3 c.c.) was added to the pasty mass obtained by dissolving benzoyl-1 : 4-naphthylenediamine (1·5 grams) in a warm mixture of glacial acetic acid and alcohol into which was introduced 1 c.c. of concentrated sulphuric acid mixed with two volumes of glacial acetic acid. The amorphous sulphate slowly changed into pale yellow plates of the diazonium salt, the precipitation of this substance being completed by the addition of absolute alcohol and ether:

0·2015 gave 18·9 c.c. nitrogen at 20° and 768 mm. N = 10·82.
0·3422 ,, 0·2177 $BaSO_4$. S = 8·74.

$C_{17}H_{13}O_5N_3S$ requires N = 11·32 ; S = 8·63 per cent.

The diazonium sulphate dissolved in water but was insoluble in alcohol or ether. The aqueous solution, when evaporated over concentrated sulphuric acid, furnished well-defined, glistening needles often one centimetre in length.

4-*Benzoylaminonaphthalene*-1-*diazonium nitrate*,

$C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot NO_3$,

was not readily obtained by direct diazotisation, but on adding dilute nitric acid to an aqueous solution of the diazonium chloride it separated in sparingly soluble yellow needles which melted and decomposed at 140—142°:

0·1688 gave 24·0 c.c. nitrogen at 24° and 778 mm. N = 16·66.

$C_{17}H_{12}O_4N_4$ requires N = 16·06 per cent.

4-*Benzoylaminonaphthalene*-1-*diazonium nitrite*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}NO_2,$$

was precipitated in yellow needles on mixing 10 per cent. aqueous solutions of the diazonium chloride and sodium nitrite; it darkened on exposure, sintered at 120°, and melted indefinitely at 145—155°:

0·1305 gave 19·0 c.c. nitrogen at 17° and 770 mm. N = 17·13.

$C_{17}H_{12}O_3N_4$ requires N = 17·50 per cent.

4-*Benzoylaminonaphthalene*-1-*diazonium chlorate* crystallised in long, iridescent, yellow needles on mixing aqueous solutions of the diazonium chloride and potassium chlorate. When heated at 130°, the salt darkened and then exploded; it also detonated on percussion or when dropped into concentrated sulphuric acid. This salt is, however, quite stable in the dry state, and is not sensitive to friction.

4-*Benzoylaminonaphthalene*-1-*diazonium perchlorate* was obtained as a pale yellow, microcrystalline precipitate on mixing cold aqueous solutions of potassium perchlorate and the diazonium chloride; it was almost insoluble in cold water and decomposed on warming with this solvent.

4-*Benzoylaminonaphthalene*-1-*diazonium chromate*, obtained as a yellowish-brown precipitate from potassium chromate and the diazonium chloride, darkened on exposure and deflagrated on heating.

4-*Benzoylaminonaphthalene*-1-*diazonium carbonate*, a yellow, microcrystalline precipitate formed on adding aqueous sodium carbonate to a solution of the diazonium chloride, was soluble in alcohol, but dissolved only sparingly in cold water. It dissolved with effervescence in hydrochloric acid and the solution developed a red coloration with alkaline β-naphthol. On heating on the water-bath, the salt darkened slightly. An estimation of carbon dioxide showed that about 90 per cent. of the substance consisted of the diazonium carbonate.

4-*Benzoylaminonaphthalene*-1-*diazonium trichloroacetate*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}CO_2{\cdot}CCl_3,$$

separated on mixing aqueous solutions of trichloroacetic acid and the diazonium chloride as a gummy mass which rapidly changed on trituration into light yellow crystals:

0·1670 gave 0·1693 AgCl. Cl = 25·07.

$C_{19}H_{12}O_3N_3Cl_3$ requires Cl = 24·44 per cent.

4-*Benzoylaminonaphthalene*-1-*diazonium thiocyanate*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}CNS,$$

was obtained as an amorphous, pale yellow precipitate, rapidly segregating into short, orange-coloured needles, on mixing dilute aqueous solutions of ammonium thiocyanate and the diazonium chloride; it darkened at 100° and melted at 103°:

0·1533 gave 0·1092 $BaSO_4$. S = 9·78.

$C_{18}H_{12}ON_4S$ requires S = 9·64 per cent.

Action of Potassium Cyanide on 4-Benzoylaminonaphthalene-1-diazonium Chloride.

1. A blood-red coloration is developed on adding aqueous potassium cyanide to the diazonium chloride dissolved in alcohol, and if the solution is sufficiently concentrated a red precipitate makes its appearance. This red product is alsc deposited when water is added at once to the red solution, whereas a yellowish-brown, finely-divided precipitate is formed when the red liquid is kept overnight before dilution with water.

2. One gram of the diazonium chloride dissolved in 10 c.c. of warm alcohol was treated with 0·25 gram of potassium cyanide (98—99 per cent. KCN) dissolved in the same solvent, and the deposition of the deep red precipitate was completed by adding 65 c.c. of water. The precipitate, which retained water persistently, weighed 0·85 gram when dry:

0·1236 gave 0·3268 CO_2 and 0·0563 H_2O. C = 72·11; H = 5·06.
0·1439 ,, 0·3804 CO_2 ,, 0·0600 H_2O. C = 72·11; H = 4·63.
0·1116 ,, 17·5 c.c. nitrogen at 17° and 762 mm. N = 18·35.
$C_{18}H_{12}ON_4$ requires C = 72·00, H = 4·00, N = 18·36 per cent.

4-*Benzoylaminonaphthalene*-1-*diazocyanide*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}CN,$$

when separating from a warm alcoholic solution appeared under the microscope ($\frac{1}{8}''$ objective) to consist of masses of fibrous curvilinear needles; it sintered and darkened at 148° and decomposed very indefinitely at about 210°. When treated with cold concentrated sulphuric acid the diazocyanide developed a deep red coloration which faded in a few minutes to a pale yellow. The partially decolorised solution, when diluted and added to alkaline β-naphthol, gave the red azo-β-naphthol. An attempt to carry out this change quantitatively showed that the acid decomposed a portion of the cyanide. The red diazocyanide differs from all the preceding diazonium salts in not coupling with alkaline β-naphthol unless treated in the foregoing manner.

3. When the diazonium chloride and potassium cyanide (in slight excess) interacted at −10°, a bright yellow precipitate was formed, but on attempting to collect a portion of this product it became tarry. The remainder of the precipitate, suspended in its mother liquor at −10°, changed in succession to bright and dark red and became distinctly crystalline. The final product did not become tarry at the ordinary temperature, and was found to be identical with the red diazocyanide. An experiment made at the temperature of liquid air showed that the diazonium chloride and potassium cyanide did not interact,

but as the temperature was slowly raised the yellow primary product was formed which finally changed into the red diazocyanide.

4. The brown substance obtained when the diazonium chloride and potassium cyanide are left overnight in alcoholic solution before the liquid is diluted with water was dried over concentrated sulphuric acid until of constant weight; it then sintered at 77° and decomposed above this temperature, evolving much gas:

0·1120 gave 0·2840 CO_2 and 0·0536 H_2O. C = 69·15; H = 5·32.
0·1362 „ 0·3414 CO_2 „ 0·0634 H_2O. C = 68·40; H = 5·17.
0·1962 „ 27·2 c.c. nitrogen at 22° and 770 mm. N = 15·93 per cent.

These data indicate the presence in the brown product of a diazocyanide isomeric with the red cyanide, but the substance was not obtained in a state of purity. This substance does not couple with alkaline β-naphthol until it has first been dissolved in cold concentrated sulphuric acid, behaving in this respect quite like the stable red cyanide. Experiments were made with the view of ascertaining the conditions under which the red cyanide becomes transformed into the brown compound. The transformation does not take place when an alcoholic solution of the red cyanide is left for some time and it is, moreover, not induced by a caustic alkali. The change is, however, determined by the presence of potassium cyanide and the reaction occurs almost quantitatively: 0·2188 gram of red cyanide in alcoholic solution with 0·09 gram of potassium cyanide, when left for sixteen hours and then treated with water containing a little sodium acetate to accelerate the deposition of the precipitate, gave 0·2104 gram of the dry brown cyanide:

0 1545 gave 22 c.c. nitrogen at 20° and 768 mm. N = 15·81.

In many experiments it was, however, found that the reaction took a different course, tarry products only being obtained.

The two diazocyanides and several of the foregoing diazonium salts were exposed to the temperature of liquid air, but in no case was there any appreciable change of colour.

Action of Alkali Hydroxides on the Diazonium Chloride.

1. *Aqueous Caustic Alkalis.*—On slowly adding dilute aqueous caustic potash to a solution of the diazonium chloride, a slight amount of dark, viscid precipitate was first formed, and after removing this and adding more alkali a yellowish-brown substance separated, which did not darken on exposure and was dried in a vacuum desiccator over sulphuric acid:

0·2354 gave 29·8 c.c. nitrogen at 20° and 762 mm. N = 14·48.

$C_{17}H_{13}O_2N_3$ requires N = 14·43 per cent.

This compound dissolved readily in caustic alkalis or in dilute acids;

in the latter solvent it reverts to the diazonium salt, which then couples with alkaline β-naphthol. The substance itself does not yield an azo-derivative, and its properties are clearly those of 4-*benzoylamino-α-naphthylnitrosoamine*, $C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot NO$.

The addition of sodium acetate to an aqueous solution of the diazonium chloride also determines the precipitation of this nitrosoamine.

2. *Alcoholic Potash.*—An aqueous solution of the diazonium chloride when added slowly to an excess of alcoholic potash produced a yellow precipitate (nitrosoamine), which immediately redissolved to a clear reddish-brown solution from which nitrogen was evolved, the liquid acquiring the odour of acetaldehyde and aldehyde resin. On diluting with water, a bulky precipitate of brown, felted needles was obtained, and this product, after repeated crystallisation, proved to be benzo-α-naphthalide (m. p. 156—157°).

*Azo-derivatives of Benzoyl-*1 : 4-*naphthylenediamine.*

4-*Benzoylaminonaphthalene*-1-*azo-β-naphthol*,
$C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH$.

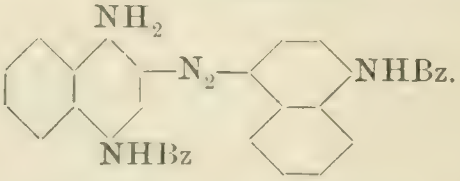
This azo-compound, when obtained by the interaction of the foregoing diazonium salts and alkaline β-naphthol, formed a brick-red precipitate, sparingly soluble in the ordinary organic solvents. When crystallised from glacial acetic acid it separated in bulky masses of red felted needles having a green reflex (m. p. 249—250°):

0·2309 gave 19·2 c.c. nitrogen at 20° and 762 mm. N = 9·53.

$C_{27}H_{19}O_2N_3$ requires N = 10·07 per cent.

The compound was insoluble in aqueous alkalis, and with concentrated sulphuric acid it developed an intense violet coloration.

4-*Benzoylaminonaphthalene*-1 : 2′-*azo*-4′-*benzoyl*-1′ : 4′-*naphthylenediamine.*



On mixing alcoholic solutions of benzoyl-1 : 4-naphthylenediamine and its diazonium chloride, a bright red precipitate was immediately formed, and after adding aqueous sodium acetate a quantitative yield of the azo-derivative was obtained. This compound, although moderately soluble in the organic solvents, was not obtained crystalline; it decomposed at 148—150°:

0·1959 gave 21·0 c.c. nitrogen at 20° and 773 mm. N = 12·48.
$C_{34}H_{25}O_2N_5$ requires N = 13·08 per cent.

With concentrated sulphuric acid, this azo-compound developed an intense violet coloration. When suspended in water and treated with acetic anhydride, it gave a red, amorphous, acetyl derivative darkening at 230° and melting at 248°. Hydrogen chloride, when passed into a glacial acetic acid solution of the azo-compound, produces an indigo-blue solution of the hydrochloride. This salt is diazotised on the addition of amyl nitrite, and its diazo-derivative can be condensed with β-naphthol or benzoyl-1 : 4-naphthylenediamine.

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CXXII.—*The Oxidation of Hydrazines by Free Oxygen.*

By Frederick Daniel Chattaway.

All chemists who have studied hydrazines have commented on the ease with which they are attacked by oxidising agents, and many have noted that they are decomposed on exposure to the air (compare Fischer, *Annalen*, 1878, **190**, 67, and Berthelot, *Compt. rend.*, 1894, **119**, 5). The course of the latter action, however, has never been systematically investigated and, except for scattered references to the fact, nothing is to be found in the literature on the subject.

Hydrazines containing a single aromatic nucleus are not, when in bulk, readily oxidised by free oxygen, as action can only take place at the surface of contact; when, however, this is much increased, as by powdering solid hydrazines or extending liquid hydrazines in thin films, oxidation takes place more rapidly, sometimes with considerable evolution of heat.

When dissolved in alcohol such hydrazines are even more slowly oxidised by free oxygen, but the action is accelerated to a remarkable degree by potassium hydroxide, the rate of oxidation varying with the temperature and with the concentration of alkali and of hydrazine in the liquid. In some cases, as, for example, with phenylhydrazine, the action may be so vigorous that on mere exposure to the air the liquid effervesces freely, owing to the rapid evolution of nitrogen.

The reaction which occurs when hydrazines are oxidised by free oxygen appears to be a general one, and takes a precisely similar course with every aromatic hydrazine of the general formula $R\cdot NH\cdot NH_2$ which has been studied.

The main action is a simple one; oxygen is absorbed, nitrogen is liberated, and the $\cdot NH\cdot NH_2$ group is replaced by hydrogen, thus:

$$2R\cdot NH\cdot NH_2 + O_2 = 2R\cdot H + 2N_2 + 2H_2O.$$

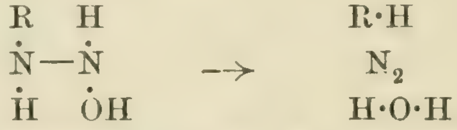
Another action accompanies this, although it takes place to a comparatively insignificant extent, and results in the formation of a hydrocarbon of the diphenyl series, thus:

$$2R\cdot NH\cdot NH_2 + O_2 = R\cdot R + H_2 + 2N_2 + 2H_2O.$$

These actions can be simply explained by assuming that when a primary aromatic hydrazine is oxidised the hydrogen of the NH_2 group is first attacked, and a hydroxyhydrazine produced, thus:

$$R\cdot NH\cdot NH_2 + O = R\cdot NH\cdot NH\cdot OH.$$

This molecular structure, however, not being stable, undergoes disruption during some period of its orbital or oscillatory motion, either in one or two stages, thus:



$$\begin{array}{ccc} R & & H \\ \dot{N} & — & \dot{N} \\ \dot{H} & & \dot{O}H \end{array} \quad \longrightarrow \quad \begin{array}{c} R\cdot H \\ N_2 \\ H\cdot O\cdot H \end{array}$$

There is no direct evidence of the actual existence of an intermediate diazene, $R\cdot N{:}NH$, which, if the transformation takes place in two stages, must momentarily be formed, unless the striking crimson colour of the solution during the reaction is due to this compound. The formation of a hydrocarbon of the diphenyl type, $R\cdot R$, is evidence that the group R has a momentary independent existence.

In all probability the action which first takes place is an addition of two hydroxyl groups to the nitrogen, which develops its higher valency. It may also be that in this action hydrogen peroxide is produced, as is the case in the atmospheric oxidation of hydrazones (Biltz and Amme, *Annalen*, 1902, **321**, 1). The question, however, cannot be decided experimentally, as hydrogen peroxide itself oxidises hydrazines, and consequently cannot be detected in the liquid.

Only hydrazines of the general formula $R\cdot NH\cdot NH_2$, containing in the cyclic residue R no substituted group, such as NO_2, capable of entering itself into action with the $\cdot NH\cdot NH_2$, in presence of alkalis, yield in this way hydrocarbons and nitrogen when oxidised.

The very small quantity of tarry matter obtained in all these reactions is probably formed by the decomposition of a diazo- or diazonium-hydroxide, produced either by the oxidation to hydroxyl groups of two hydrogen atoms attached to nitrogen in the original hydrazine followed by elimination of water, or by oxidation of the first formed diazene before transformation.

EXPERIMENTAL.

Oxidation of Hydrazines by Free Oxygen.

Although phenylhydrazine is fairly readily attacked by free oxygen, action can only take place at the surface of contact, and consequently it is not rapid when the hydrazine is in bulk. It can, however, be rendered so by increasing the surface, as by exposing the liquid to the action of the gas in a thin layer. To investigate the action, sheets of filter paper were soaked with freshly distilled phenylhydrazine and placed in large stoppered bottles filled with oxygen gas. Under these conditions rapid oxidation occurred, the bottles quickly became warm from the heat evolved, and a dew collected on the sides. The liquid covering the paper, at first pale yellow, became stained reddish-brown, and this colour deepened as oxidation proceeded. The bottles were kept at the ordinary temperature screened from light for eight days, at the end of which time the oxygen had completely disappeared, its place being taken by a greater volume of nitrogen. In one experiment in which the volumes of the two gases were measured, the nitrogen obtained was found to 1·8 times the volume of the oxygen used. The contents of the bottles on distillation with steam, yielded pure benzene, the amount of which corresponded as closely as could be expected with the volume of oxygen used, and varied between 80 and 90 per cent. of that theoretically required for the relation $C_6H_6:O$. The very small amount of dark-coloured tarry matter formed remained in the distillation flask with the excess of hydrazine used, the benzene distilling over much more readily than the latter.

The oxidation of *o*- and *p*-tolylhydrazine, *p*-bromophenylhydrazine and of *α*- and *β*-naphthylhydrazine was also investigated with precisely similar results, toluene, bromobenzene, and naphthalene being respectively produced, together with a volume of nitrogen roughly double that of the oxygen used.

This oxidation accounts for the apparent disappearance of phenylhydrazine when spilled, and for the odour of hydrocarbon or hydrocarbon derivative noticed when other compounds of this nature are kept in loosely stoppered bottles. The naphthylhydrazines, when so kept, appear to become transformed into a somewhat discoloured porous mass of naphthalene, the nitrogen produced escaping unnoticed.

Oxidation of Hydrazines by Free Oxygen, in presence of Alcoholic Potash.

Potassium hydroxide and, to a less extent, sodium hydroxide very much accelerate the rate at which hydrazines are oxidised; in some cases this is so much increased that on merely exposing a solution of the hydrazine in alcoholic potash for a short time to the air, the temperature rises and nitrogen is given off so rapidly that the liquid effervesces vigorously. The products are the same as when the hydrazines are oxidised by simple exposure to oxygen, and as the actions take place in solution they can be studied more easily.

Oxidation of Phenylhydrazine by Free Oxygen in presence of Alcoholic Potash.—If a warm saturated solution of potassium hydroxide in absolute alcohol is mixed with an equivalent quantity of phenylhydrazine and allowed to stand for a long period carefully protected from the air, and especially if a stick of fused potassium hydroxide is placed in the liquid, large, rhombic, colourless crystals separate, consisting of a potassium derivative of phenylhydrazine analogous to the sodium derivative investigated by Michaelis (*Ber.*, 1886, **19**, 2448, and *Annalen*, 1889, **252**, 267) and having probably a similar structure, $C_6H_5\cdot NK\cdot NH_2$. No nitrogen is evolved nor any colour change produced, no decomposition whatever taking place. If, however, such a mixture of phenylhydrazine and alcoholic potash is exposed to the air, rapid oxidation takes place, the rate varying with the concentration of the potassium hydroxide and of the hydrazine. With a very small quantity of potash present, or in dilute solution, oxidation is comparatively slow, scarcely any effervescence due to escaping nitrogen being noticed when the liquid is exposed to the air at the ordinary temperature. The rate of oxidation increases as the amount of potash and hydrazine present increases until it reaches a maximum, when a saturated solution of potash is mixed with an equimolecular quantity of phenylhydrazine; action is then extremely rapid. Further increase in the amount of potash used, with the consequent increase in the amount of alcohol, does not increase, but appears to diminish, the rate of oxidation, possibly owing to dilution hindering the rate at which the oxygen comes into contact with the hydrazine.

In studying the oxidation of phenylhydrazine in presence of alcoholic potash, a solution made by mixing an approximately 4*N*-solution of potassium hydroxide in alcohol with an equimolecular amount of phenylhydrazine was used.

On exposing this solution to the air at the ordinary temperature, it immediately begins to give off bubbles of nitrogen, a strong odour of benzene is noticed, and the liquid becomes warm. As the temperature rises the rate at which nitrogen is evolved increases, until the liquid effervesces rapidly. At first, although nitrogen is being freely evolved, there is little change of colour, but after the liberation of gas has proceeded for a few minutes a slight red tint becomes apparent, which, as oxidation proceeds, very much deepens, the colour of the liquid ultimately becoming deep crimson. After some ten to thirty minutes, depending on the temperature and the way the liquid is brought into contact with the air, the evolution of nitrogen ceases, and further contact with air causes no effervescence in the liquid. Slow decomposition of the coloured compound, however, still goes on, and on prolonged exposure to the air the crimson shade disappears, and an orange-coloured liquid is left. On allowing the alcohol and the benzene formed to evaporate, and water to be absorbed, or on adding a comparatively small quantity of the latter, a viscid, orange-red liquid separates. The potassium hydroxide is not altered in the action, and can be recovered from the residue unchanged in amount, except by a slight conversion into carbonate, which is probably formed mainly or entirely from the carbon dioxide of the air.

The course of the chief reaction which takes place in the oxidation of phenylhydrazine can be better followed if oxygen is used, and if the oxidation is carried out in a closed vessel. The phenomena observed are precisely those which take place on simple exposure to air; the same brilliant crimson colour is developed, and the same products are formed, these being nitrogen, benzene, and a very little of the orange-red, viscid material. If $4N$-alcoholic potash is mixed with the equivalent amount of phenylhydrazine and the solution shaken vigorously with oxygen in a large tap funnel about a quarter filled, the nitrogen formed being allowed to escape and the oxygen being continually replaced as it is used up, the temperature of the liquid rises rapidly and generally reaches to 65—75°.

In order to estimate the amount of nitrogen liberated by a given volume of oxygen, a quantity of the latter gas, usually 20 c.c., was placed in a Lunge's nitrometer, about 5 c.c. of $4N$-alcoholic potash were added, and then, after carefully rinsing the upper cup with alcohol, 2 c.c. of phenylhydrazine were run in. The liquids must be mixed in the nitrometer itself, as on the shortest exposure to the air after mixture a certain amount of oxygen is absorbed, which later causes a liberation of nitrogen, and so gives an incorrect result.

On shaking the alkaline hydrazine solution with the oxygen in the nitrometer, rapid absorption takes place, but as nitrogen is almost at once evolved this is soon apparently checked, being actually more than balanced by the nitrogen liberated; the diminution in bulk initially observed generally amounts to about half the volume of the oxygen added. As the evolution of nitrogen continues the volume of gas in the nitrometer increases, until in about half an hour no further augmentation of bulk occurs. The volume of nitrogen obtained, which varies slightly in different experiments, approaches closely, but never quite reaches, double the volume of oxygen used. In a large number of experiments, using each time 20 c.c. of oxygen, the volume of nitrogen obtained varied between 38 and 39 c.c.

Very little reddening takes place if excess of phenylhydrazine and alcoholic potash is used, but if the partly oxidised liquid is again treated with a fresh quantity of oxygen, the crimson colour makes its appearance.

To estimate the amount of benzene formed, a known amount of phenylhydrazine dissolved in excess of alcoholic potash was heated in a distilling apparatus, and a slow stream of oxygen passed in as long as any benzene distilled over with the alcohol. The distillate was collected in a receiver cooled by ice, and the benzene obtained by diluting it with water. In a number of experiments an average yield of 95 per cent. of the theoretical amount of pure benzene was obtained.

To estimate the amount of red tarry matter formed a rapid stream of air, freed from carbon dioxide, was drawn by a water pump through a mixture of 100 grams of phenylhydrazine, 120 grams of 4*N*-alcoholic potash and 200 grams of alcohol at the ordinary temperature. As oxidation progressed the liquid became warm, and in half an hour the temperature had risen from 9° to 30°, the liquid had become deep crimson in colour, and the odour of benzene was very noticeable. The passage of air was continued for fifty hours, until the crimson colour had completely disappeared and a deep orange-coloured liquid of a peculiar odour was left. This liquid was then exposed to the air at the ordinary temperature until the alcohol had disappeared and the potash had absorbed sufficient water to cause the orange product to separate The latter was then extracted with ether, the solution dried, and the ether evaporated; 2·8 grams of a reddish-orange, viscid liquid were obtained. This dissolved in glacial acetic acid without change; it gave a dirty green colour when mixed with concentrated hydrochloric and a vivid green with sulphuric acid. On reduction with tin and hydrochloric acid a small quantity of tar separated. On precipitating the tin by hydrogen sulphide and making alkaline with potash, a small quantity of a viscous, basic substance was precipitated. This was boiled with acetic anhydride and a solid derivative obtained, but from the very small quantity available no crystalline compound could be isolated.

The alkaline liquid left after extracting the substance just described with ether was digested with a little animal charcoal, acidified with hydrochloric acid, and again extracted with ether; on evaporating the ether, the merest trace of a reddish-brown tar of a peculiar odour was left, showing that no weighable amount of phenol had been produced.

To ascertain if the presence of water affected the course of the reaction, a similar experiment was made, using 100 grams of phenylhydrazine, 120 grams of alcoholic potash, 100 grams of alcohol, and 100 grams of water. It was found that in this case oxidation was not quite so rapid, but otherwise the course of the reaction appeared to be the same. The alkaline residue, acidified as before, yielded 0·8 gram of reddish-brown tar, which after some time partially solidified. It gave no violet colour with ferric chloride, and when pressed on porous porcelain left a very small amount of a white, crystalline solid which melted at 125°. This solid gave a bromine derivative, but owing to the small amount formed neither the solid nor its bromine derivative could be recrystallised or further examined.

Diphenyl is also produced in small amount when phenylhydrazine is directly oxidised thus by free oxygen. Five hundred grams of phenylhydrazine were mixed with alcoholic potash and oxidised in a current of air as already described. After allowing the alcohol freely to evaporate, the alkaline residue, together with the tarry matter, was distilled in steam for a considerable time. A small quantity of diphenyl was thus obtained, which was recognised by its appearance, odour, and melting point.

Oxidation of p-*Bromophenylhydrazine by Free Oxygen.*

p-Bromophenylhydrazine is less readily oxidised by free oxygen than the unsubstituted compound. The rate of oxidation, whilst without doubt mainly affected by the sparing solubility of the bromo-compound in alcoholic potash, appears to be lessened by the primary oxidation product breaking down less rapidly than the corresponding unsubstituted one. It is, as in the former case, much increased by heating. On suspending powdered *p*-bromophenylhydrazine in $4N$-alcoholic potash and exposing the mixture to the air no noticeable effervescence due to escape of nitrogen occurs until the liquid is heated. Experiments carried out in a Lunge's nitrometer, however, show that the action, although slow, follows the same course as with phenylhydrazine, and that the volume of nitrogen liberated by a given volume of oxygen approaches double that of the latter gas used. The yield of bromobenzene was ascertained as before by oxidising a known weight of *p*-bromophenylhydrazine dissolved in excess of a boiling solution of alcoholic potash by passing in a slow stream of oxygen; pure bromobenzene separated from the colourless distillate on dilution, and a yield varying from 98 to 99 per cent. of the theoretical was obtained. The amount of tarry matter formed was trifling, and proportionally much smaller than that produced in the oxidation of phenylhydrazine.

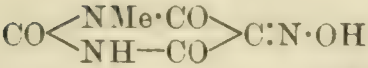
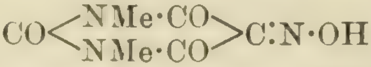
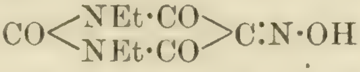
Oxidation of o- *and* p-*Tolylhydrazine by Free Oxygen.*

The tolylhydrazines are oxidised in presence of alcoholic potash even more slowly than *p*-bromophenylhydrazine. When either is mixed with an equivalent amount of 4*N*-alcoholic potash and exposed to the air in shallow vessels, although the odour of toluene can soon be recognised, the liquid does not become tinged with red, nor are bubbles of nitrogen visibly given off until several hours have elapsed. Even when the solution is heated and vigorously shaken with oxygen, action is not at all rapid. The course of the reaction, however, is the same as in the other cases, nitrogen and toluene being produced together with a very small quantity of tarry matter. Oxidation is best effected by passing a slow stream of oxygen through a boiling solution of the hydrazine in alcoholic potash. The ortho-compound is, in these circumstances, oxidised somewhat more rapidly than the para. In both cases a colourless distillate is collected, from which, on diluting with water, pure toluene separates. The amount of toluene obtained is in each case nearly theoretical.

α- and *β*-Naphthylhydrazines are similarly oxidised by free oxygen, naphthalene and nitrogen being produced.

CXXIII.—*Studies in the Barbituric Acid Series. I.* 1 : 3-*Diphenylbarbituric Acid and some Coloured Derivatives.**

By Martha Annie Whiteley.

The alkyl violuric acids hitherto described have contained the substituents in the 1- or the 1 : 3-positions. These acids, namely, methyl-violuric acid,  $CO<\begin{array}{l}NMe\cdot CO\\ NH-CO\end{array}>C:N\cdot OH$ (Andreasch, *Monatsh.*, 1900, **21**, 281), dimethylvioluric acid,  $CO<\begin{array}{l}NMe\cdot CO\\ NMe\cdot CO\end{array}>C:N\cdot OH$ (Techow, *Ber.*, 1894, **27**, 3082), and diethylvioluric acid,  $CO<\begin{array}{l}NEt\cdot CO\\ NEt\cdot CO\end{array}>C:N\cdot OH$ (Sembritzki, *Ber.*, 1897, **30**, 1814), are colourless compounds, yielding the red or violet alkali and blue ferrous salts characteristic of cyclic compounds containing the α-oximino-ketone complex.

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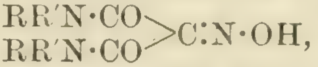
* This paper corresponds with the abstracts in Proc., 1906, **22**, 200; 1907, **23**, 180 and 203.

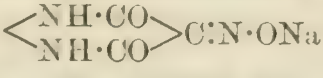
It has been shown in earlier papers (Whiteley, Trans., 1900, **77**, 1040; 1903, **83**, 24; Proc., 1904, **20**, 92) that whilst *iso*nitrosomalonamide and its di- or tetra-substituted derivatives,

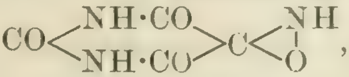
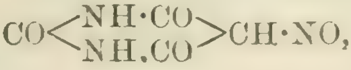
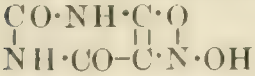

$$\begin{array}{l}RR'N\cdot CO\\ RR'N\cdot CO\end{array}>C:N\cdot OH,$$

give yellow alkali and blue or violet ferrous salts characteristic of open chain α-oximino-ketones, certain of the *aryl* derivatives are themselves yellow or exist as yellow and colourless dynamic isomerides. In explanation of this isomerism, it was suggested that the coloured acid and salt are true oximes and the colourless acid an *iso*oxime.

The similarity in properties and constitution of violuric acid and *iso*nitrosomalonamide led to the preparation of 1 : 3-diphenylvioluric acid in order to ascertain whether an aryl violuric acid would exhibit dynamic isomerism similar to that already mentioned. The new acid proves to be a well-defined, colourless, crystalline compound whether prepared by the action of ethyl nitrite or nitrosyl chloride on 1 : 3-diphenylbarbituric acid, or by decomposing with acids the red sodium salt obtained by the action of sodium nitrite on the barbituric acid, and the evidence of its existence in a coloured isomeric form is unsatisfactory. It is true, however, that a red syrup is obtained when 5 : 5-dibromo-1 : 3-diphenylbarbituric acid and hydroxylamine hydrochloride are allowed to interact in absolute alcoholic solution either alone or with the addition of sodium acetate, and that the red syrup when dissolved in sodium hydroxide yields a red solution which gives the deep blue coloration with ferrous salts characteristic of violuric acids.

At the present time the view seems generally to be accepted that the coloured salts of violuric acid are oximes of the type,


$$<\begin{array}{l}NH\cdot CO\\ NH\cdot CO\end{array}>C:N\cdot ONa$$

(compare Lowry, *Brit. Assoc. Report,* 1904, 222; Hartley, Trans., 1905, **87**, 1816; Baly, Trans., 1906, **89**, 981); whereas the colourless acid is regarded as the *iso*oxime,  $CO<\begin{array}{l}NH\cdot CO\\ NH\cdot CO\end{array}>C<\begin{array}{l}NH\\ \mid\\ O\end{array}$, by Lowry (*loc. cit.*), as the nitroso-compound,  $CO<\begin{array}{l}NH\cdot CO\\ NH.CO\end{array}>CH\cdot NO$, by Hartley (*loc. cit.*), and as belonging to a new type represented by the formula  $\begin{array}{l}\mathrm{CO{\cdot}NH{\cdot}C{\cdot}O}\\ \mathrm{NH{\cdot}CO{-}C{\cdot}N{\cdot}OH}\end{array}$ by Baly (*loc. cit.*).

In the absence of analytical evidence in favour of any of these formulæ, the *iso*oximic structure for violuric acid and its 1 : 3-dialkyl or diaryl derivatives may be provisionally accepted. In common with the nitroso-formula, it has the typical structure, $\cdot\underset{\cdot\ \cdot\ \cdot\ \cdot\ \cdot}{\mathrm{C{\cdot}\dot{C}{\cdot}C}}\cdot$, of a colourless derivative of the chromophoric complex, $\cdot\underset{\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot}{\mathrm{C{\cdot}C{\cdot}C}}\cdot$; but, unlike the nitroso-formula, does not preclude the existence of "nitrogen ethers," of which several have been described in the case of certain *iso*oximes (compare Dunstan and Goulding, Trans., 1901, **79**, 628; Forster, Trans., 1904, **85**, 896).

The violuric acid, however, is only one of the large number of derivatives of 1 : 3-diphenylbarbituric acid described in this paper; these compounds may be conveniently considered under the following headings:

I. Synthesis of 1 : 3-diphenyluric acid.

II. Condensation of 1 : 3-diphenylbarbituric acid with aldehydes and dichloro-ketones.

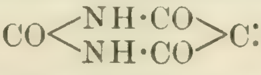
III. Condensation of 1 : 3-diphenylbarbituric acid or its 5-alkyl derivatives with aromatic diazonium chlorides.

IV. Condensation of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid with phenylhydrazine or its β-substituted derivatives.

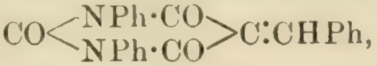
I. *Synthesis of* 1 : 3-*Diphenyluric Acid.*

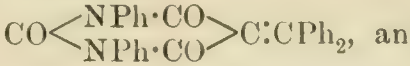
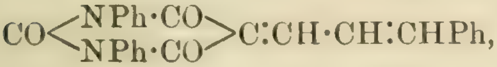
The work described in this section calls for no comment, Fischer's method for the synthesis of alkyl uric acids (*Ber.*, 1895, **28**, 3135) being followed throughout.

II. *Condensation of* 1 : 3-*Diphenylbarbituric Acid with Aldehydes or Dichloro-ketones.*

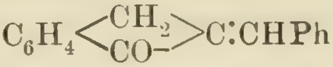
Conrad and Reinbach (*Ber.*, 1901, **34**, 1339) found that barbituric acid by condensation with aromatic aldehydes forms derivatives of the type  $\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{C{:}CHR}$ and described the benzylidene and *o*-nitrobenzylidene derivatives as colourless, the cinnamylidene and furfurylidene derivatives being yellow. Weinschenk (*Ber.*, 1901, **34**, 1685) independently obtained similar results, and in addition found that *p*-hydroxybenzylidene- and *p*-dimethylaminobenzylidene-barbituric acid are canary-yellow and orange-red respectively.

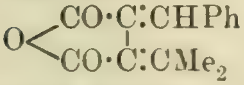
The experiments described later show that the 1 : 3-diphenyl homologue, like barbituric acid, condenses readily with aromatic aldehydes or with dichloro-ketones, and that the benzylidene,


$$CO\!<\!\begin{matrix}NPh\cdot CO\\ NPh\cdot CO\end{matrix}\!>\!C{:}CHPh,$$

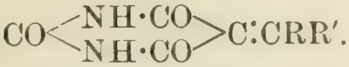
the diphenylmethylene,  $CO\!<\!\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}\!>\!C{:}CPh_2$, and cinnamylidene,  $CO\!<\!\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}\!>\!C{:}CH\cdot CH{:}CHPh$, derivatives are sulphur-yellow, bright yellow, and orange respectively. It was observed, however, that when a solution of the benzylidene compound in acetone, ethyl acetate, or alcohol was allowed to evaporate spontaneously, the crystalline product was a mixture of sulphur-yellow with a relatively small quantity of entirely colourless needles, which melted sharply at 214°, as did a mixture of the two.

Two cases of isomerism among benzylidene derivatives have been described which present analogies with that shown by 1 : 3-diphenyl-5-benzylidenebarbituric acid. 2-Benzylidene-1-hydrindone,

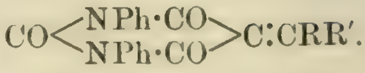

$$C_6H_4\!<\!\begin{matrix}CH_2\\ CO-\end{matrix}\!>\!C{:}CHPh$$

(Kipping, Trans., 1894, **65**, 499), forms pale yellow plates and prisms which melt at 109—110°, solidify, and then melt partially at 90° and completely at 109—110°, that is to say, the isomerides differ in melting point, but not in colour. With δ-phenyl-*αα*-dimethylfulgide,  $O\!<\!\begin{smallmatrix}CO\cdot C{:}CHPh\\ |\\ CO\cdot C{:}CMe_2\end{smallmatrix}$ (Stobbe, *Ber.*, 1905, **38**, 3893), the analogy is much more striking. This substance exists in two forms, one yellow and the other colourless, each melting at 115—116° and convertible into the other by the action of solvents or of light. Stobbe does not offer any explanation of this isomerism, but even if this be found in spacial considerations, it may not be out of place to point out that stereoisomerism is not possible in the case of 1 : 3-diphenyl-5-benzylidenebarbituric acid.

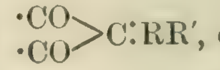
The nature of the relationship between the constitution and colour of compounds of the benzylidenebarbituric acid type is still obscure, but the following conclusions seem to be justified; for convenience sake the colour of the various benzylidene derivatives are given in the table :

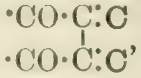
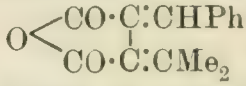
Derivatives of Barbituric Acid,  $CO\!<\!\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}\!>\!C{:}CRR'$.

Benzylidene-	barbituric	acid	colourless
o-Nitrobenzylidene-	,,	,,	,,
Cinnamylidene-	,,	,,	yellow
Furfurylidene-	,,	,,	,,
p-Hydroxybenzylidene-	,,	,,	,,
p-Dimethylaminobenzylidene-	,,	,,	,,

Derivatives of Diphenylbarbituric Acid,  $\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh\cdot CO}}{\mathrm{NPh\cdot CO}}{>}\mathrm{C{:}CRR'}$.

1 : 3-Diphenylbenzylidene-	barbituric acid	*α*-yellow *β*-colourless
1 : 3-Diphenyldiphenylmethylene-	„ „	yellow
1 : 3-Diphenylcinnamylidene-	„ „	orange-yellow

Each of these compounds contains the complex  $\genfrac{}{}{0pt}{}{\cdot\mathrm{CO}}{\cdot\mathrm{CO}}{>}\mathrm{C{:}RR'}$, consisting of three chromophores (two carbonyl radicles and one ethylene linking), yet each is colourless or coloured according to the nature of the radicles R and R′. From the results thus summarised it would seem that when R is hydrogen and R′ phenyl or its ortho-substituted derivative the product is usually colourless, but that it is yellow when R′ is a para-substituted derivative of phenyl (compare Weinschenk, *loc. cit.*), or a more highly unsaturated radicle such as that afforded by cinnamaldehyde or furfuraldehyde. When both R and R′ are phenyl groups the compound is yellow.

The analogy between these compounds and the fulgides is very striking. Stobbe has shown (*Annalen*, 1906, **349**, 338) that the complex,  $\begin{matrix}\cdot\mathrm{CO\cdot C{:}}\mathbf{C}\\ \quad\;\mid\\ \cdot\mathrm{CO\cdot C{:}}\mathbf{C}\end{matrix}$, consisting of four chromophores (two conjugated ethylene linkings and two carbonyl radicles) present in each of the fulgides, is powerless to produce coloured derivatives until a sufficient number of phenyl or more highly unsaturated groups are associated with the ethylene carbon atoms shown in black type. For example, δ-phenyl-*αα*-dimethylfulgide,  $\mathrm{O}{<}\begin{matrix}\mathrm{CO\cdot C{:}CHPh}\\ \qquad\mid\\ \mathrm{CO\cdot C{:}CMe_2}\end{matrix}$, exists in two forms, one yellow and one colourless, whilst its nitro-derivatives are sulphur-yellow, bright yellow, or bright orange, according as the nitro-group is substituted respectively in the ortho-, meta-, or para-position; and δδ-diphenyl-*αα*-dimethylfulgide is lemon-yellow.

III. *Condensation of* 1 : 3-*Diphenylbarbituric Acid or its* 5-*Alkyl-substituted Derivatives with Aromatic Diazonium chlorides.*

IV. *Condensation of* 5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric Acid with Phenylhydrazine or its β-substituted Derivatives.*

(*a*) 1 : 3-Diphenylbarbituric acid condenses readily with benzenediazonium chloride to form a yellow compound which can also be obtained by the interaction of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid and phenylhydrazine. This compound, like its nitro-derivative obtained from 1 : 3-diphenylbarbituric acid and *p*-nitrobenzenediazonium chloride, is not decomposed by prolonged boiling with alcohol and hydrochloric acid, and is insoluble in sodium carbonate solution.

(*b*) Condensation products are also obtained from 5-benzyl- or 5-diphenylmethyl-1 : 3-diphenylbarbituric acid and benzene- or *p*-nitro-benzenediazonium chloride. These compounds are likewise yellow, but are readily decomposed by boiling with alcohol and hydrochloric acid, the compound obtained from 1 : 3-diphenyl-5-benzylbarbituric acid yielding under these conditions 1 : 3-diphenyl-5-benzylbarbituric acid, nitrogen, phenetole, and phenol.

(*c*) The interaction of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid under suitable conditions and *as*-diphenyl-, phenylmethyl-, or phenylbenzyl-hydrazine leads to the formation of a series of compounds which are yellow or red, or have the remarkable property of existing as a pair of dynamic isomerides. These compounds, like those described under (*a*), are not decomposed when boiled with alcohol and hydrochloric acid.

It is therefore clear from the method of preparation that, unless a wandering of the benzyl or diphenylmethyl radicle has occurred, the compounds described under (*b*) are azo-derivatives of the type $\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CRN{:}NR'}$, and the readiness with which they are hydrolysed by alcohol and hydrochloric acid affords strong evidence in favour of this constitution. The preparation and hydrolysis respectively of 5-benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid can therefore be represented by equations I and II :

$$\text{I.}\quad \mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CH\cdot CH_2Ph + C_6H_5\cdot N_2Cl} =$$

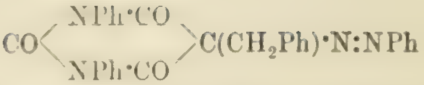
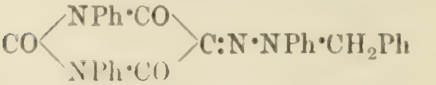
$$\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C(CH_2Ph)\cdot N{:}NPh + HCl.}$$

$$\text{II.}\quad \mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C(CH_2Ph)\cdot N{:}NPh + HCl} =$$

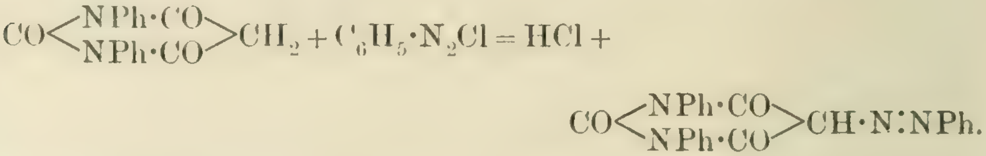
$$\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CH\cdot CH_2Ph} + \left[\mathrm{C_6H_5\cdot N_2Cl}\right]$$

$$\mathrm{C_6H_5\cdot N_2Cl} + \begin{cases}\mathrm{EtOH}\\ \mathrm{H_2O}\end{cases} = \begin{cases}\mathrm{C_6H_5\cdot OEt}\\ \mathrm{C_6H_5\cdot OH}\end{cases} + \mathrm{N_2 + HCl.}$$

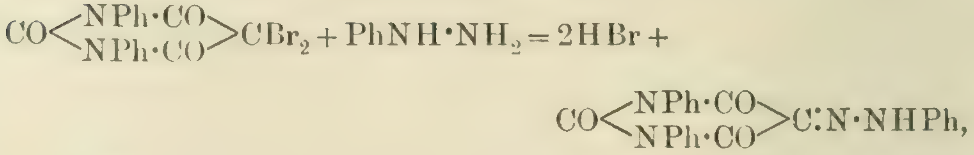
That the compounds described under (*c*) must be regarded as hydrazones of the type $\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C{:}N\cdot NRR'}$, seems to follow from their method of preparation, and from the important fact that the substance obtained by the interaction of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid and *as*-phenylbenzylhydrazine is isomeric with the 5-benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid already described. The differences between the two compounds are summarised in the following table :

	M. p.	Colour.
 $\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{C(CH_2Ph)\cdot N{:}NPh}$ ...... 5-Benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid.	170—171°	Yellow
 $\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{C{:}N\cdot NPh\cdot CH_2Ph}$ ...... 1 : 3-Diphenylalloxanphenylbenzylhydrazone.	α 130—131° β 130—131°	Red Yellow

The constitution of the compounds described under (*a*) still remains to be discussed. From the two methods of preparation they may be either azo-derivatives (equation I) or hydrazones (equation II).

I. 

$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{CH_2 + C_6H_5\cdot N_2Cl = HCl +}$$
$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{CH\cdot N{:}NPh.}$$

II. 

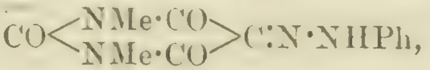
$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{CBr_2 + PhNH\cdot NH_2 = 2HBr +}$$
$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}\right>\mathrm{C{:}N\cdot NHPh,}$$

and the difficulty has to be met that a "wandering" of a hydrogen atom has occurred during one of the reactions. Possibly the examination of the alkyl derivatives of the compounds now in progress may throw some light on this problem. Meanwhile the compounds may be provisionally regarded as hydrazones, because in common with the hydrazones described under (*c*) they are not decomposed by prolonged boiling with alcohol and hydrochloric acid, and are insoluble in sodium carbonate solution.

The difficulty of discriminating between the azo and hydrazone constitution in the case of compounds which from their methods of preparation may have one or the other formula is no new one. Richard Meyer (*Ber.*, 1891, 24, 1241), for example, found that phenylhydrazonemesoxalic acid was identical with benzeneazomalonic acid, but was unsuccessful in attempting to prepare the diethyl ester which would be soluble or insoluble in alkali carbonates according as it had the azo, $\mathrm{(CO_2Et)_2CH\cdot N{:}NPh}$, or the hydrazone,

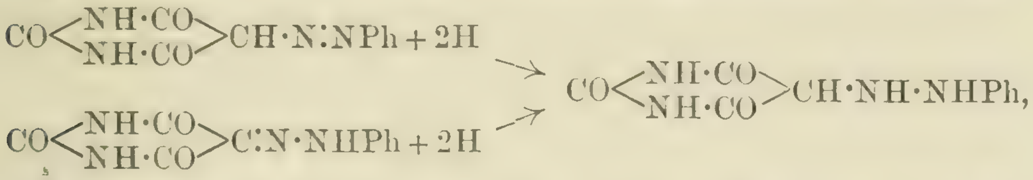
$\mathrm{(CO_2Et)_2C{:}N\cdot NHPh}$,

constitution. Kühling (*Ber.*, 1891, 24, 4140; 1898, 31, 1972), who prepared alloxanphenylhydrazone, $\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{C{:}N\cdot NHPh}$, by the action of phenylhydrazine on alloxan, and by the interaction of benzenediazonium chloride and barbituric acid, assigned to it the hydrazone constitution, because, although itself soluble in alkali carbonates, the corresponding dimethyl derivative,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{NMe{\cdot}CO}\end{matrix}\right>\mathrm{C{:}N{\cdot}NHPh},$$

was insoluble in alkalis. The reduction of the alloxanphenylhydrazone to uramil and aniline by tin and hydrochloric acid advanced by Kühling as an argument in favour of this constitution is not conclusive, however, as the same result might be expected if the compound had the azo-configuration; for assuming the reduction to proceed normally, the hydrazine would be formed as an intermediate product in both cases:

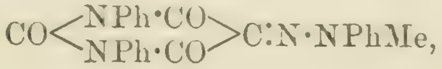


$$\begin{matrix}\mathrm{CO}\left<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right>\mathrm{CH{\cdot}N{:}NPh}+2\mathrm{H} & \searrow & \\ & & \mathrm{CO}\left<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right>\mathrm{CH{\cdot}NH{\cdot}NHPh},\\ \mathrm{CO}\left<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right>\mathrm{C{:}N{\cdot}NHPh}+2\mathrm{H} & \nearrow & \end{matrix}$$

and this on further reduction might break down into uramil and aniline.

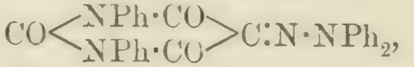
A similar problem was investigated by Japp and Klingemann (Trans., 1888, **53**, 519), who found that α-phenylazopropionic acid, $\mathrm{CO_2H{\cdot}CHMe{\cdot}N{:}NPh}$, was identical with phenylhydrazonepyruvic acid, $\mathrm{CO_2H{\cdot}CMe{:}N{\cdot}NHPh}$. In this case, the hydrazone constitution of the compound was fully established by the reduction of its alkyl-substituted derivatives.

Dynamic Isomerism among the Hydrazones of 1 : 3-*Diphenylalloxan.* —1 : 3-Diphenylalloxanphenylmethylhydrazone,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{NPh{\cdot}CO}\end{matrix}\right>\mathrm{C{:}N{\cdot}NPhMe},$$

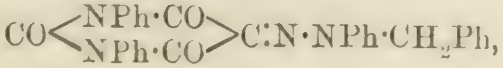
and 1 : 3-diphenylalloxandiphenylhydrazone,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{NPh{\cdot}CO}\end{matrix}\right>\mathrm{C{:}N{\cdot}NPh_2},$$

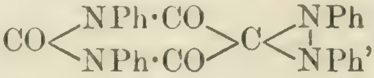
are well-defined crystalline compounds, each of which exists in two forms, one stable and one labile, differing from one another only in colour and crystalline form. The stable form of the phenylmethyl derivative consists of bright orange-red prisms with a blue reflex, and the labile form of yellow needles; whilst the stable form of the diphenyl derivative consists of yellow needles, and the labile form of red prisms. The stable passes into the labile form by the action of certain solvents, but most readily by pressure, thus the yellow diphenyl derivative leaves a bright red streak when rubbed on a smooth surface, and the red phenylmethyl derivative, similarly treated, gives a bright yellow streak.

1 : 3-Diphenylalloxanphenylbenzylhydrazone,

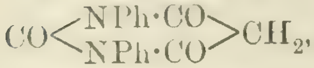


$$\mathrm{CO}\left<\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{NPh{\cdot}CO}\end{matrix}\right>\mathrm{C{:}N{\cdot}NPh{\cdot}CH_2Ph},$$

unlike the two preceding compounds, yields a *labile* form which can be isolated in a state of purity; it consists of bright red, brilliant prisms soluble in warm benzene forming a red solution, which becomes yellow on cooling and deposits the *stable* form as bright yellow needles; from toluene solutions a mixture of the red prisms and yellow needles is obtained.

The examination of these and related derivatives is being continued in the hope that some light may be thrown on the nature of the isomerism of these hydrazones, the inferences drawn in this paper concerning the constitution of these compounds being purely negative in character. Difference in structure arising from stereoisomerism is precluded in these symmetrical compounds; the azo-structure is also inadmissible from considerations already mentioned; and, lastly, a formula of the type suggested by Armstrong and Robertson (Trans., 1905, 87, 1295) for the colourless hydrazones of camphorquinone seems to be inapplicable in this case, because in all probability the isomeric compound,  $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{NPh}_{NPh}$, will also prove to be colourless.

Experimental.

I. *Synthesis of* 1 : 3-*Diphenyluric Acid.*—1 : 3-*Diphenylbarbituric acid*,  $CO<^{NPh\cdot CO}_{NPh\cdot CO}>CH_2$, is obtained by the direct condensation of malonyl chloride with *s*-diphenylcarbamide or by the action of phosphoryl chloride on a mixture of malonic acid and *s*-diphenylcarbamide. The first method of preparation gives the better yield, but the cost of materials is more than twice that entailed by the second.

First Method.—A mixture of 34 grams of malonyl chloride (1 mol.), 55 grams of finely powdered *s*-diphenylcarbamide (1 mol.), and 150 c.c. of pure chloroform dried over sodium was boiled in a reflux apparatus on a water-bath during four hours. The solid product after being separated by filtration and washed with chloroform weighed 36 grams and consisted of unchanged *s*-diphenylcarbamide (13·4 grams), and 1 : 3-diphenylbarbituric acid (20 grams). These were separated by means of sodium carbonate solution in which the acid dissolved readily and was recovered by the addition of hydrochloric acid to the solution. A further quantity of 18·3 grams of 1 : 3-diphenylbarbituric acid was isolated from the chloroform mother liquor by spontaneous evaporation to dryness and extraction of the syrupy residue with alcohol. In addition to these substances the alcoholic filtrate and washings contained ethyl malonate and a crystalline compound melting at 160° which has not yet been identified.

Second Method.—This is a modification of the method employed by

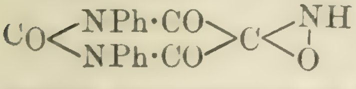
Grimaux for the preparation of barbituric acid (*Compt. rend.*, 1879, **88**, 85) and by Sembritzki for the preparation of malonyldiethylcarbamide (*Ber.*, 1897, **30**, 1814), and consists in heating a mixture of malonic acid and *s*-diphenylcarbamide in a chloroform solution of phosphoryl chloride. The best results were obtained when a mixture of 30 grams of phosphoryl chloride (2 mols.), 10 grams of malonic acid (1 mol.), 20 grams of *s*-diphenylcarbamide (1 mol.), and 100 c.c. of dry chloroform was heated in a reflux apparatus at a temperature just below the boiling point of the mixture during six hours. The chloroform was allowed to evaporate spontaneously from the solution, and the residual syrup, after being left in contact with alcohol for several hours to decompose the excess of phosphoryl chloride, was poured on to ice. A white solid separated which consisted of *s*-diphenylcarbamide (5·6 grams), 1 : 3-diphenylbarbituric acid (10·2) grams, and the acetyl derivative of the acid (6·5 grams). The two last dissolved readily in sodium carbonate solution, and after precipitation by hydrochloric acid were separated from one another by fractional crystallisation from alcohol in which the 1 : 3-diphenylbarbituric acid is sparingly, and the acetyl derivative readily, soluble.

1 : 3-*Diphenylbarbituric acid* crystallises from alcohol in colourless, prismatic needles, melts at 238°, and dissolves in each of the usual organic solvents with the exception of ether and light petroleum :

0·1900 gave 0·4788 CO_2 and 0·0766 H_2O. C = 68·70 ; H = 4·48.
0·2624 gave 22·6 c.c. moist nitrogen at 15·5° and 761·4 mm. N = 10·08.
$C_{16}H_{12}O_3N_2$ requires C = 68·57 ; H = 4·28 ; N = 10·02 per cent.

The *acetyl* derivative, $C_{16}H_{11}O_3N_2Ac$, melting at 150°, will be described in a later paper dealing with the acyl and 5 : 5-dialkyl derivatives of 1 : 3-diphenylbarbituric acid.

5-iso*Nitroso*-1 : 3-*diphenylbarbituric Acid* (1 : 3-*Diphenylvioluric Acid*),



$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C<\begin{matrix}NH\\|\\O\end{matrix}$$

.—To prepare this substance, 1 : 3-diphenylbarbituric acid dissolved in dry chloroform is mixed with 1 molecular proportion of freshly prepared ethyl nitrite (Dunstan, *Pharm. J.*, 1887, **18**, 861) in alcoholic solution (44 per cent.) in a closed flask. The solution, originally deep red, becomes pale yellow after about two days, and on rapid evaporation of the chloroform in the cold, deposits the 1 : 3-diphenylvioluric acid in a crystalline form. The yield is 85 per cent. of the calculated amount. 5-iso*Nitroso*-1 : 3-*diphenylbarbituric acid* crystallises from absolute alcohol in colourless needles, which become red at 200°, and melt and decompose at 227° ; it is soluble in each of the ordinary organic solvents with the exception of ether :

4 T 2

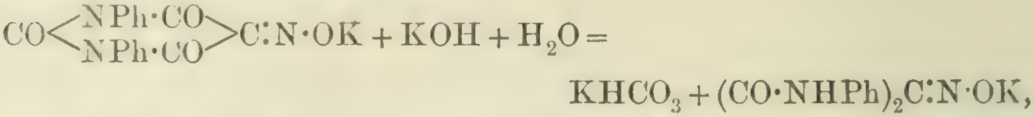
0·2925 gave 34·2 c.c. moist nitrogen at 18·5° and 763·3 mm. N = 13·53.
$C_{16}H_{11}O_4N_3$ requires N = 13·59 per cent.

The *potassium* salt, $C_{16}H_{10}O_4N_3K,2\frac{1}{2}H_2O$, obtained in violet prisms on mixing alcoholic solutions of equivalent quantities of potassium hydroxide and the acid just described, is readily soluble in water and crystallises from concentrated aqueous solutions in long, purple, hydrated prisms:

0·2869 lost 0·0326 at 110—115° and gave 0·0647 K_2SO_4. $H_2O = 11·36$; K = 10·13.
$C_{16}H_{10}O_4N_3K,2\frac{1}{2}H_2O$ requires $H_2O = 11·48$; K = 9·96 per cent.

The addition of ferrous sulphate solution to an aqueous solution of the potassium salt produces a deep blue coloration, but all attempts to isolate the ferrous compound were unsuccessful.

When the potassium salt is suspended in 30 per cent. potassium hydroxide solution it is decomposed; there is formed the potassium salt of *iso*nitrosomalonanilide,



$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NPh{\cdot}CO}}{>}\mathrm{C{:}N{\cdot}OK} + \mathrm{KOH} + \mathrm{H_2O} = \mathrm{KHCO_3} + (\mathrm{CO{\cdot}NHPh})_2\mathrm{C{:}N{\cdot}OK},$$

and on acidifying the mixture *iso*nitrosomalonanilide melting at 141° is precipitated (Whiteley, Trans., 1903, **83**, 35). 1:3-Dimethylvioluric acid is similarly decomposed by alkalis (Whiteley, Trans., 1903, **83**, 23).

The *piperidine* salt, $C_{16}H_{11}O_4N_3,C_5H_{11}N$, crystallises from alcohol and water in bright rose-red needles which melt and decompose at 218°:

0·2646 gave 32·9 c.c. moist nitrogen at 21·5° and 765·6 mm. N = 14·23.
$C_{21}H_{22}O_4N_4$ requires N = 14·21 per cent.

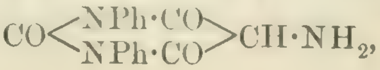
The *aniline* salt, $C_{16}H_{11}O_4N_3,C_6H_5{\cdot}NH_2$, forms purple, crystalline scales or flattened needles; it is insoluble in alcohol and dissociated by water:

0·2162 gave 26 c.c. moist nitrogen at 18·5° and 759 mm. N = 13·85.
$C_{22}H_{18}O_4N_4$ requires N = 13·93 per cent.

The *acetyl* derivative, $C_{16}H_{10}O_4N_3Ac$, obtained by the action of acetyl chloride on 5-*iso*nitroso-1:3-diphenylbarbituric acid in glacial acetic acid solution, forms colourless prisms, melts and decomposes at 245°, is insoluble in ethyl or methyl alcohol or benzene, but dissolves in the other organic solvents:

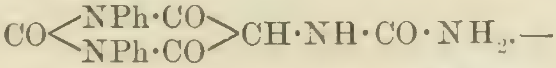
0·2193 gave 30·3 c.c. moist nitrogen at 20° and 763·5 mm. N = 11·95.
$C_{18}H_{13}O_5N_3$ requires N = 11·96 per cent.

-*Amino*-1 : 3-*diphenylbarbituric acid* (1 : 3-*diphenyluramil*),

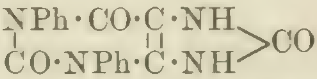


$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NPh{\cdot}CO}}{>}\mathrm{CH{\cdot}NH_2},$$

is obtained in the form of its hydriodide when the *iso*nitroso-acid is reduced by means of hydriodic acid. Four grams of 5-*iso*nitroso-1 : 3-diphenylbarbituric acid are gradually added to 10 c.c. of hydriodic acid (sp. gr. 1·94) at – 15°, the mixture being ground in a mortar during the operation. The dark red, semi-solid mass is then allowed to attain the temperature of the laboratory, phosphonium iodide added in small quantities with a few drops of water until a clear pale yellow solution is obtained and the solution left in a desiccator over soda-lime for two or three days. The uramil hydriodide forms crystalline nodules, and the yield is quantitative. It dissolves readily in cold water, but is rapidly dissociated into hydrogen iodide and 5-amino-1 : 3-diphenylbarbituric acid; this separates in thin, silky, colourless needles which, after crystallisation from alcohol, melt at 97°, but redden so rapidly in the air that the compound could not be obtained sufficiently pure for analysis.

1 : 3-*Diphenyl-ψ-uric Acid*, 
$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2$.—When 5-amino-1 : 3-diphenylbarbituric acid (1 mol.) is mixed with potassium cyanate ($1\frac{1}{2}$ mols.) in aqueous solution, it dissolves rapidly, forming a deep purple solution which becomes pale yellow after being heated on the steam-bath for fifteen minutes, and on the addition of excess of hydrochloric acid to the cooled solution yields 1 : 3-diphenyl-ψ-uric acid. This acid forms colourless needles, melts and decomposes at 217°, and is insoluble in alcohol, ethyl acetate, or water, but can be crystallised from glacial acetic acid:

0·2076 gave 0·4526 CO_2 and 0·0780 H_2O. C = 59·46; H = 4·17.
0·1862 ,, 26·7 c.c. moist nitrogen at 19·5° and 763·4 mm. N = 16·52.
$C_{17}H_{14}O_4N_4$ requires C = 60·35; H = 4·14; N = 16·57 per cent.

1 : 3-*Diphenyluric Acid*, 
$\begin{matrix}NPh\cdot CO\cdot C\cdot NH\\|\qquad\qquad ||\\CO\cdot NPh\cdot C\cdot NH\end{matrix}>CO$.—When 4 grams of 1 : 3-diphenyl-ψ-uric acid are heated in a reflux apparatus on a steam-bath for eight hours with 60 grams of 25 per cent. hydrochloric acid, a solution is obtained which, when cold, deposits colourless crystals weighing 2·8 grams, and consisting of 1 : 3-diphenyluric acid (2·4 grams) and *s*-diphenylcarbimide* (0·4 gram). The two products are readily separated by means of sodium carbonate solution in which the uric acid is soluble.

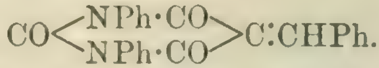
1 : 3-*Diphenyluric acid* crystallises from a mixture of alcohol and water in long, silky needles, which melt only at a temperature above 306°.

0·2802 gave 0·6483 CO_2 and 0·0970 H_2O. = 63·1; H = 3·85.
0·1614 ,, 25 c.c. moist nitrogen at 20·25° and 754·7 mm. N = 17·58.
$C_{17}H_{12}O_3N_4$ requires C = 63·75; H = 3·75; N = 17·50 per cent.

The formation of *s*-diphenylcarbamide in this reaction is probably due to hydrolysis, as 1 : 3-diphenylbarbituric acid also yields *s*-diphenylcarbamide* when similarly treated with hydrochloric acid.

II. *Condensation of* 1 : 3-*Diphenylbarbituric Acid with Aldehydes and Dichloroketones.*

1 : 3-*Diphenyl*-5-*benzylidenebarbituric Acid*,



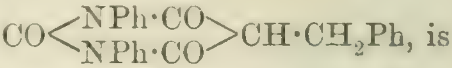
$CO\left<\begin{matrix}NPh\cdot CO\\ NPh\cdot CO\end{matrix}\right>C:CHPh$.

—When 1 : 3-diphenylbarbituric acid (1 mol.) is boiled with an alcoholic solution of benzaldehyde ($1\frac{1}{8}$ mols.) a deep yellow solution is produced from which crystals begin to separate after a few minutes. The liquid is then allowed to cool and deposits the pure benzylidene compound in pale yellow, flattened needles melting at 214°. The yield is quantitative.

1 : 3-*Diphenyl*-5-*benzylidenebarbituric acid* is insoluble in methyl alcohol, ether, light petroleum, or carbon tetrachloride, and only sparingly soluble in ethyl alcohol, but dissolves readily in the other ordinary organic solvents. On complete evaporation of the solution in ethyl acetate, acetone, or alcohol, a mixture of yellow and colourless needles is obtained. Each of these forms melts sharply at 214°, as does also a mixture of the two:

0·2501 gave 16·4 c.c. moist nitrogen at 14·5° and 757·8 mm. N = 7·67.
$C_{23}H_{16}O_3N_2$ requires N = 7·61 per cent.

1 : 3-*Diphenyl*-5-*benzylbarbituric acid*,



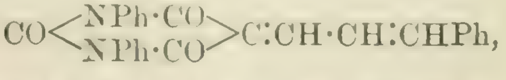
$CO\left<\begin{matrix}NPh\cdot CO\\ NPh\cdot CO\end{matrix}\right>CH\cdot CH_2Ph$,

is readily obtained when the corresponding benzylidene compound is reduced by boiling in acetic acid solution with its own weight of zinc dust until colourless. The solution is cooled, filtered from the zinc acetate and excess of zinc, and poured on to ice. The benzyl derivative separates as a flocculent, white precipitate which after a few hours changes into a soft, spongy mass, and gradually becomes hard and crystalline; the yield is quantitative.

1 : 3-*Diphenyl*-5-*benzylbarbituric acid* is very readily soluble in all the ordinary organic solvents except light petroleum or carbon tetrachloride; it crystallises from the last-named solvent or from a mixture of benzene and light petroleum (60—80°) in brilliant prismatic crystals which melt indefinitely at 140—145°:

After being dried at 110° until the weight was constant:
0·1836 gave 0·5047 CO_2 and 0·0826 H_2O. C = 74·95; H = 5·00.
$C_{23}H_{18}O_3N_2$ requires C = 74·60; H = 4·86 per cent.

1 : 3-*Diphenyl*-5-*cinnamylidenebarbituric acid*,



$CO\left<\begin{matrix}NPh\cdot CO\\ NPh\cdot CO\end{matrix}\right>C:CH\cdot CH:CHPh$, obtained in a similar manner to the benzylidene compound, forms bright orange-yellow needles which melt and decompose at 268°. It dissolves readily in acetic acid, toluene, or cold chloroform, but is insoluble or nearly so in the other ordinary solvents; it is most conveniently crystallised from a mixture of chloroform and alcohol:

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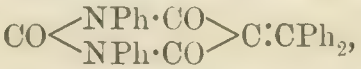
* M. p. 236°. Found N = 13·24; $C_{13}H_{13}ON_2$ requires N = 13·21 per cent.

0·2373 gave 14·8 c.c. moist nitrogen at 22·5° and 763·8 mm. N = 7·08.
$C_{25}H_{18}O_3N_2$ requires N = 7·11 per cent.

This compound is readily reduced by zinc and acetic acid, yielding a colourless acid, which dissolves in sodium carbonate solution and is very readily soluble in all ordinary organic solvents except light petroleum.

1 : 3-*Diphenyl-5-diphenylmethylenebarbituric acid*,



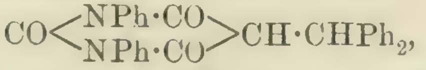
$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C{:}CPh_2,$$

is obtained when 1 : 3-diphenylbarbituric acid is boiled with excess of benzophenone dichloride. 25·8 grams of benzophenone dichloride (1·7 mols.), prepared according to Mackenzie's modification of Kekulé and Franchimont's method (Trans., 1896, **69**, 986), mixed with 18 grams of 1 : 3-diphenylbarbituric acid (1 mol.) and about 10 c.c. of dry chloroform, is gently boiled in a reflux apparatus; hydrogen chloride is copiously evolved, and after removal of the chloroform by distillation the heating is continued until the contents of the flask become completely solid on cooling. A yellow, crystalline cake is obtained which, after treatment with cold alcohol, yields 23·8 grams of pure 1 : 3-diphenyl-5-diphenylmethylenebarbituric acid, and 13·7 grams of benzophenone can be recovered from the alcoholic washings.

1 : 3-*Diphenyl-5-diphenylmethylenebarbituric acid* forms deep yellow, prismatic crystals melting at 264°, and is soluble in the ordinary organic solvents except ether and light petroleum; it is, however, decomposed on prolonged boiling with alcohol or acetic acid, yielding 1 : 3-diphenylbarbituric acid and benzophenone, and is therefore most conveniently recrystallised by adding cold alcohol to a warm chloroform solution of the compound:

0·1398 gave 0·4012 CO_2 and 0·0592 H_2O. C = 78·23; H = 4·70.
0·3000 „ 15·5 c.c. dry nitrogen at 17° and 772 mm. N = 6·21.
$C_{29}H_{20}O_3N_2$ requires C = 78·36; H = 4·50; N = 6·31 per cent.

1 : 3-*Diphenyl-5-diphenylmethylbarbituric acid*,



$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>CH\cdot CHPh_2,$$

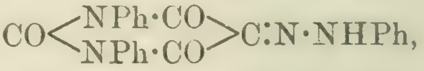
is obtained by boiling the preceding compound in acetic acid with its own weight of zinc dust until the solution becomes colourless; the clear, hot liquid is then decanted into cold water when the reduced compound is precipitated as a white, crystalline powder, a further quantity being recoverable from the zinc residues. The yield is quantitative.

1 : 3-*Diphenyl-5-diphenylmethylbarbituric acid* is soluble in all the ordinary organic solvents with the exception of carbon tetrachloride, ether, or light petroleum, and is obtained in colourless, brilliant, well-developed prisms melting at 205—206° on adding alcohol to a hot chloroform solution. Like the corresponding benzyl derivative, the compound dissolves readily in aqueous sodium carbonate and is precipitated unchanged on acidifying the alkaline solution :

0·2156 gave 0·6140 CO_2 and 0·0968 H_2O. $C = 77·70$; $H = 4·99$.
0·3591 ,, 19·2 c.c. moist nitrogen at 15° and 782·6 mm. $N = 6·44$.
$C_{29}H_{22}O_3N_2$ requires $C = 78·03$; $H = 4·93$; $N = 6·28$ per cent.

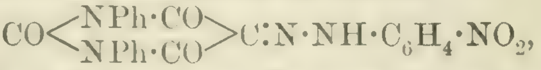
III. *Condensation of* 1 : 3-*Diphenylbarbituric Acid or its* 5-*Alkyl-substituted Derivatives with Aromatic Diazonium Chlorides.*

The method adopted for the preparation of the compounds described under this section was as follows. A dilute solution of the diazonium chloride formed from 1 mol. of the aromatic amine (aniline or *p*-nitroaniline), was slowly added to an alkaline solution of 1 mol. of the barbituric acid or its alkyl derivative, and the finely divided yellow precipitate of the condensation product collected, washed, dried on a porous plate, and recrystallised from a suitable solvent.

1 : 3-*Diphenylalloxanphenylhydrazone*,  $\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C{:}N\cdot NHPh}$, dissolves in all the ordinary organic solvents except ethyl or methyl alcohol, ether, carbon tetrachloride, or light petroleum, and crystallises from dilute acetic acid or from a mixture of chloroform and alcohol in bright yellow needles which melt and decompose at 265°. The compound is not decomposed by prolonged boiling with a mixture of alcohol and concentrated hydrochloric acid in equal volumes, and on reduction with zinc dust and acetic acid yields a product which is soluble in water and does not contain aniline :

0·1670 gave 20·5 c.c. moist nitrogen at 17° and 772·4 mm. $N = 14·48$.
$C_{22}H_{16}O_3N_4$ requires $N = 14·58$ per cent.

1 : 3-*Diphenylalloxan*-p-*nitrophenylhydrazone*,

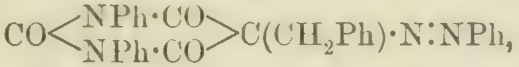


$$\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C{:}N\cdot NH\cdot C_6H_4\cdot NO_2},$$

prepared from 1 : 3-diphenylbarbituric acid and *p*-nitroaniline, is soluble in the usual organic solvents except alcohol, ether, light petroleum, or carbon tetrachloride, and crystallises from acetic acid in well-developed, yellow prisms with a purple reflex, which melt and decompose at 274° :

0·1546 gave 22·3 c.c. moist nitrogen at 21·5° and 759·2 mm. N = 16·37.
$C_{22}H_{15}O_5N_5$ requires N = 16·32 per cent.

5-*Benzeneazo*-1 : 3-*diphenyl-5-benzylbarbituric acid*,



$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C(CH_2Ph)\cdot N\colon NPh,$$

obtained from aniline and 1 : 3-diphenyl-5-benzylbarbituric acid, dissolves sparingly in ethyl or methyl alcohol, is soluble in the other ordinary organic solvents except ether, light petroleum, or carbon tetrachloride, and crystallises from a mixture of chloroform and alcohol, or benzene and light petroleum, in bright yellow, well-developed prisms which melt and decompose at 170—171° :

0·2188 gave 0·5847 CO_2 and 0·0945 H_2O. C = 72·87 ; H = 4·80.
0·1897 „ 18·8 c.c. moist nitrogen at 19° and 780·2 mm. N = 11·70.
$C_{29}H_{22}O_3N_4$ requires C = 73·42 ; H = 4·64 ; N = 11·81 per cent.

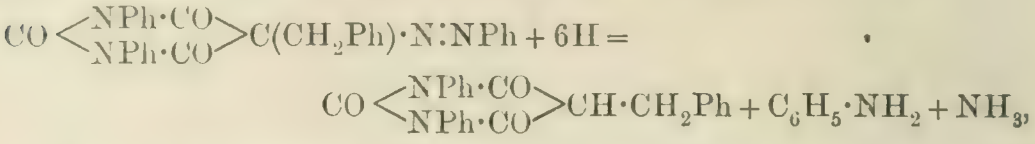
Hydrolysis of 5-*Benzeneazo*-1 : 3-*diphenyl-5-benzylbarbituric Acid.*

5-Benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid is slowly decomposed by the prolonged action of concentrated hydrochloric acid in the cold, with the formation of 1 : 3-diphenyl-5-benzylbarbituric acid. If, however, it is warmed with alcohol containing one-sixth of its volume of concentrated hydrochloric acid a very vigorous action takes place. Nitrogen is evolved and on addition of water to the alcoholic solution, 1 : 3-diphenyl-5-benzylbarbituric acid is precipitated together with a syrup which has the pungent odour of a mixture of phenylhydrazine and phenol. As, however, the product does not reduce Fehling's solution, it cannot contain phenylhydrazine. Phenol, recognised by its tribromo-derivative is, however, present, and probably phenetole as well.

That the reaction is quantitative may be judged from the results of an experiment in which a known weight of 5-benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid was hydrolysed and the nitrogen evolved measured in a volumeter :

0·5164 gave 24·6 c.c. moist nitrogen at 19° and 750 mm. N = 5·40.
$C_{29}H_{22}O_3N_4$ requires loss of nitrogen = 5·90 per cent.

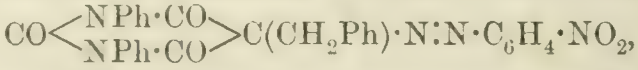
Reduction of 5-*Benzeneazo*-1 : 3-*diphenyl-5-benzylbarbituric Acid.*— The reduction was effected by boiling 20 grams of the acid suspended in alcohol with zinc dust and 10 c.c. of glacial acetic acid until the solution became colourless. After removal of the zinc acetate and excess of zinc by filtration, and spontaneous evaporation of the filtrate, a solid was left mixed with a syrup which had the odour of phenol and gave the Liebermann reaction. When triturated with dilute sodium hydroxide ammonia was evolved, and almost the whole of the solid passed into solution, which was then extracted with ether. The alkaline solution on the addition of hydrochloric acid gave 10 grams of 1 : 3-diphenyl-5-benzylbarbituric acid, and when dry hydrogen chloride was passed through the ethereal extract crystals of aniline hydrochloride were deposited. The following equation represents the reduction of 5-benzeneazo-1 : 3-diphenyl-5-benzylbarbituric acid:



$$\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NPh\cdot CO}}{\mathrm{NPh\cdot CO}}>\mathrm{C(CH_2Ph)\cdot N{:}NPh} + 6\mathrm{H} =$$
$$\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NPh\cdot CO}}{\mathrm{NPh\cdot CO}}>\mathrm{CH\cdot CH_2Ph} + \mathrm{C_6H_5\cdot NH_2} + \mathrm{NH_3},$$

and if the assumption is made that reduction is accompanied by hydrolysis, the presence of phenol among the products of the reaction is explained.

5-p-*Nitrobenzeneazo*-1 : 3-*diphenyl*-5-*benzylbarbituric acid*,



$$\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NPh\cdot CO}}{\mathrm{NPh\cdot CO}}>\mathrm{C(CH_2Ph)\cdot N{:}N\cdot C_6H_4\cdot NO_2},$$

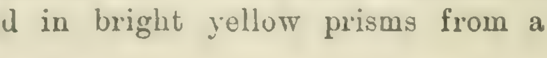
prepared from 1 : 3-diphenyl-5-benzylbarbituric acid and *p*-nitroaniline, is soluble in all the ordinary organic solvents except ether and light petroleum. It crystallises from a mixture of alcohol and chloroform partly in well-developed, bright yellow prisms, which decompose at 181—182°, and partly in tufts of pale yellow needles, which also decompose at 181—182° and are converted into the prismatic form on recrystallisation from a mixture of alcohol and chloroform:

0·1666 gave 0·4083 CO_2 and 0·0640 H_2O. C = 66·83; H = 4·27.
0·1957 ,, 21·9 c.c. moist nitrogen at 15·5° and 766·9 mm. N = 13·26.
$C_{29}H_{21}O_5N_5$ requires C = 67·04; H = 4·05; N = 13·48 per cent.

5-p-*Nitrobenzeneazo*-1 : 3-*diphenyl*-5-*benzylbarbituric acid* is more stable than the corresponding benzene derivative; it is not readily hydrolysed by boiling with alcohol and hydrochloric acid, but is reduced by the action of zinc dust and acetic acid, yielding 1 : 3-diphenyl-5-benzylbarbituric acid. This product was identified by conversion into the *p*-nitrobenzeneazo-derivative which melted and decomposed at 176°:

0·2111 gave 23·6 c.c. moist nitrogen at 16° and 771·8 mm. N = 13·29.

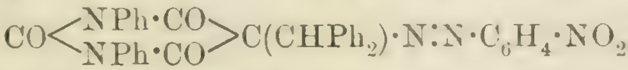
5-*Benzeneazo*-1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid*,



$$\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NPh\cdot CO}}{\mathrm{NPh\cdot CO}}>\mathrm{C(CHPh_2)\cdot N{:}NPh},$$

prepared from aniline and 1 : 3-diphenyl-5-diphenylmethylbarbituric acid, is deposited in bright yellow prisms from a boiling methyl alcoholic solution of the crude compound. These crystals melt and decompose at 160°, but attempts to recrystallise them from a mixture of acetone and methyl alcohol, benzene and light petroleum, or alcohol and chloroform were unsuccessful, for in the place of a uniform substance a mixture of yellow and colourless crystals was obtained. The colourless crystals when isolated from the mixture melted at 205—206°, and were identical with 1 : 3-diphenyl-5-diphenylmethylbarbituric acid.

5-p-*Nitrobenzeneazo*-1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid*,



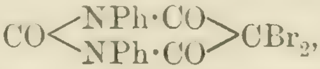
$$CO<{NPh\cdot CO \atop NPh\cdot CO}>C(CHPh_2)\cdot N:N\cdot C_6H_4\cdot NO_2,$$

is obtained as a yellow powder when *p*-nitrobenzenediazonium chloride is added to an alkaline solution of 1 : 3-diphenyl-5-diphenylmethylbarbituric acid. It dissolves readily in the cold in all the ordinary organic solvents except light petroleum, but separates in bright yellow, prismatic crystals when a methyl-alcoholic solution is warmed, and is readily purified by dissolving the crystals in cold chloroform and adding methyl alcohol (2 vols.) to the filtered solution. It crystallises in canary yellow, highly-refractive prisms, and melts and decomposes at 175° :

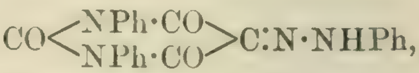
0·2137 gave 21·7 c.c. moist nitrogen at 14·2° and 749·8 mm. N = 11·78.
0·2810 in 15·73 benzene gave a depression 0·160°. M.W. = 592.
$C_{35}H_{25}O_5N_5$ requires N = 11·76 per cent. M.W. = 595.

5-p-*Nitrobenzeneazo*-1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid* is readily reduced by zinc and acetic acid, yielding 1 : 3-diphenyl-5-diphenylmethylbarbituric acid melting at 205—206°.

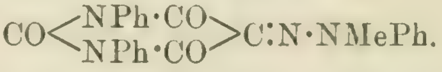
IV. *Condensation of Phenylhydrazine or its β-substituted Derivatives with* 5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric Acid.*

5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric acid*,  $CO<{NPh\cdot CO \atop NPh\cdot CO}>CBr_2$, is obtained when a mixture of barbituric acid (1 mol.) and bromine (2 mols.) is dissolved in acetic acid and warmed on the steam-bath for an hour and then poured on to broken ice ; the yield is quantitative. The precipitated dibromo-compound dissolves readily in all the ordinary organic solvents except light petroleum, and crystallises from a hot benzene solution in brilliant, well formed, elongated, colourless prisms containing 1 mol. of benzene, which is retained during recrystallisation from alcohol, and only completely eliminated on fusion of the crystals at 152° ; the benzene-free compound melts at 160°. The specimen used for analysis was dried at 105° until the weight was constant, and the bromine determined by a modification of Stephanoff's method (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 12) :

0·5062 gave 0·3660 AgBr. Br = 30·77.
0·4529 ,, 21·8 c.c. moist nitrogen at 15·5° and 755 mm. N = 5·59.
$C_{16}H_{10}O_3N_2Br_2,C_6H_6$ requires Br = 31·10 ; N = 5·43 per cent.

1 : 3-Diphenylalloxanphenylhydrazone,  $\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NPh{\cdot}CO}}{>}\mathrm{C{:}N{\cdot}NHPh}$, is formed when 5 : 5-dibromo-1 : 3-diphenylbarbituric acid (1 mol.) is warmed with phenylhydrazine ($1\frac{1}{2}$ mols.) in acetic acid solution, and separates from the cold solution in bright yellow needles which melt and decompose at 264°, and do not depress the melting point of the compound prepared from 1 : 3-diphenylbarbituric acid and benzene diazonium chloride (page 1344).

1 : 3-*Diphenylalloxanphenylmethylhydrazone*,

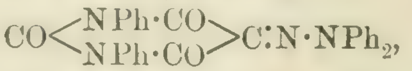


$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NPh{\cdot}CO}}{>}\mathrm{C{:}N{\cdot}NMePh}.$$

When an alcoholic solution of *as*-phenylmethylhydrazine (1 mol.) is added to a warm alcoholic solution of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid (1 mol.), a bright red colour is developed and the liquid becomes hot and sometimes even boils. As it cools the pure hydrazone separates in bright orange-red crystals which melt and decompose at 175°, the yield being 82 per cent. of the calculated amount. 1 : 3-*Diphenylalloxanphenylmethylhydrazone* dissolves in all the ordinary organic solvents except ether or light petroleum, and when recrystallised from a mixture of alcohol and chloroform separates into the two forms already described (page 1337). The first and larger crops of crystals consists of the orange-red prisms of the *stable* form of the compound, the *labile* form being obtained on complete evaporation of the mother liquor in bright yellow needles which melt and decompose at 175°. When the orange-red prisms are ground in an agate mortar they yield a bright yellow powder, or when pressed on a smooth surface show a bright yellow streak :

0·2745 gave 33·8 c.c. moist nitrogen at 20·5° and 758 mm. N = 14·01.
$C_{23}H_{18}O_3N_4$ requires N = 14·07 per cent.

1 : 3-*Diphenylalloxandiphenylhydrazone*,



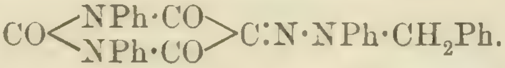
$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NPh{\cdot}CO}}{>}\mathrm{C{:}N{\cdot}NPh_2},$$

prepared by a similar method to that just described, forms bright yellow needles, which melt and decompose at 254—255°, and constitute the *stable* form of the compound. It is insoluble in ether, and dissolves sparingly in ethyl or methyl alcohol, ethyl acetate, acetone, or carbon tetrachloride, forming orange-yellow solutions which deposit the yellow needles on evaporation. It dissolves readily in acetic acid, chloroform, benzene, or nitrobenzene, forming deep red solutions, from which, however, the yellow needles separate on evaporation.

The yellow crystals, when ground in an agate mortar, give rise to an orange-red powder, and when pressed on a smooth surface produce a bright red streak; these facts, taken in conjunction with the change of colour in solution, seem to justify the conclusion that the labile form of this compound is red, but so far it has not been obtained free from the stable yellow form. It may be mentioned, however, that on one occasion when a small quantity of the hydrazone was being prepared, a mixture of yellow needles and red prisms separated from the solution; the prisms became yellow at 200°, and melted and decomposed at 252°:

0·2875 gave 31·3 c.c. moist nitrogen at 24° and 759·3 mm. N = 12·19.
$C_{28}H_{20}O_3N_4$ requires N = 12·17 per cent.

1 : 3-*Diphenylalloxanphenylbenzylhydrazone*,



$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C:N\cdot NPh\cdot CH_2Ph.$$

—Some difficulty was experienced in effecting the condensation of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid and *as*-phenylbenzylhydrazine hydrochloride. When acetic acid solutions of the two substances were mixed, a very vigorous action occurred, and a pungent tear-exciting vapour was produced, but the only compound isolated from the mixture was 1 : 3-diphenylalloxanphenylhydrazone, which melted and decomposed at 264° [0·2535 gave 32 c.c. moist nitrogen at 23·5° and 768·1 mm. N = 14·35 (theory requires N = 14·4 per cent.)].

It was found, however, that by adding phenylbenzylhydrazine hydrochloride (1 mol.) to a warm methyl-alcoholic solution of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid (1 mol.), the reaction proceeded normally, the colour changing to a deep red and the solution becoming very hot. The hydrazone thus obtained formed brilliant red prisms which melted and decomposed at 130°. The yield amounted only to 50 per cent. of the calculated quantity.

1 : 3-*Diphenylalloxanphenylbenzylhydrazone* is insoluble in ether, light petroleum, or carbon tetrachloride, but dissolves readily in all the other ordinary organic solvents, forming deep red solutions from which, except in the case of benzene and toluene, the *labile* form of the hydrazone is deposited as red prisms. The red benzene solution becomes yellow on cooling and rapidly deposits the *stable* form of the hydrazone as bright yellow needles which become red at 120°, melt and decompose at 130°, and when dissolved in methyl alcohol form a red solution from which the red prisms of the *labile* form separate on

evaporation. From a toluene solution, on the other hand, a mixture of the red prisms and yellow needles is obtained:

0·2213 gave 23 c.c. moist nitrogen at 22·75° and 768·6 mm. N = 11·85.
0·1418 in 18·85 benzene gave a depression 0·089°. M.W. = 448.
$C_{29}H_{22}O_3N_4$ requires N = 11·81 per cent. M.W. = 474.

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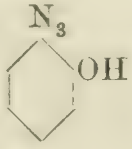
CXXIV.—*Aromatic Azoimides. Part II. Ortho- and Meta-hydroxyphenylazoimides.*

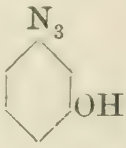
By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

BY experience gained from the investigation of *p*-hydroxyphenylazoimide (this vol., p. 855), the preparation of the isomeric substances has been much facilitated. We find that the hypothetical additive compound of the diazotised aminophenol with hydroxylamine is more stable in presence of excess of sodium carbonate than was originally supposed, and although potassium hydroxide accelerates the transformation of this compound into azoimide, we have abstained from adding free alkali, preferring to maintain the temperature of the well-stirred liquid at zero during an interval of many hours. By this modification the hydroxyphenylazoimide is produced more slowly, but in a form more readily freed from associated materials. In the case of the meta-compound it is necessary to add a quadruple proportion of hydroxylamine in order to secure a satisfactory yield; with the quantity which sufficed in previous experiments, the principal product consists of a brick-red azo-compound, and the yield of hydroxyphenylazoimide is only one-third of the optimum.

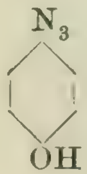
A comparison of the three hydroxyphenylazoimides has revealed some interesting points. The almost invariable rule that a para-compound is the least fusible of the series is exactly inverted by the compounds under consideration:



Decomposes at 145° without fusion.

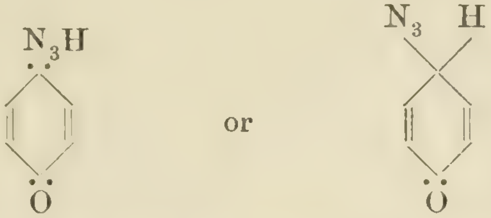


M. p. 36·5°.



Oil.

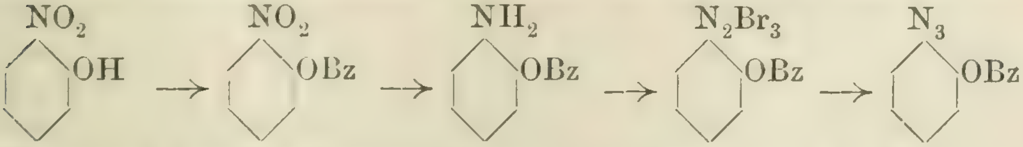
We have already suggested a reason for the low melting point of *p*-hydroxyphenylazoimide, which we believe quickly changes into a mixture of the enolic form, represented above, with a varying proportion of the ketonic isomeride, which may be either quinonoid or quinolic,



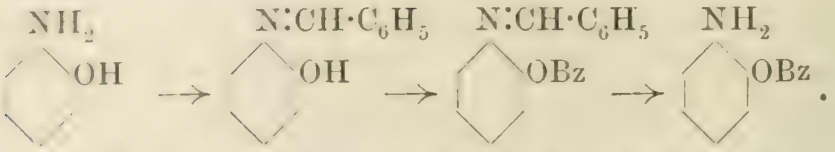
This is indicated, not only by the alteration which the phenol itself undergoes in the desiccator, but by the remarkable colour change which occurs when the potassium derivative is warmed in alcoholic or aqueous solution. The meta-compound does not display these properties, and we believe it to be normal, whilst the high melting point of the ortho-derivative is perhaps explained by its bimolecular structure, a peculiarity which appears from the molecular weight determination and from the persistence with which it retains a one-half molecule of water of crystallisation. In order to render the identity of these compounds less doubtful, we have made a comparison of the three benzoyl derivatives and their *p*-nitro-compounds, finding that in these two series the melting point relationships are quite normal:

	Ortho. M. p.	Meta. M. p.	Para. M. p.
Benzoyl derivative	45°	50°	81°
p-Nitrobenzoyl derivative	101	136	169—170

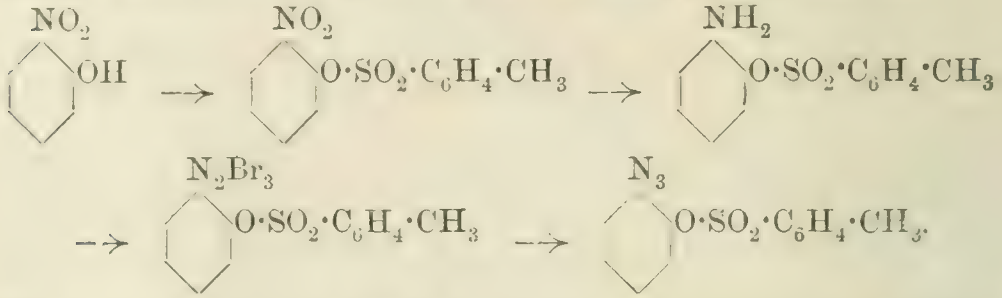
Owing to the unusual properties of *o*-hydroxyphenylazoimide, we thought it desirable also to prepare one of its derivatives by an independent method as we did in the case of *p*-benzoxyphenylazoimide (*loc. cit.*, p. 866). From this point of view it was natural to attempt the preparation from *o*-nitrophenol instead of the *p*-nitrophenol employed in the case quoted, but the readiness with which the benzoic ester of *o*-nitrophenol yields the anhydro-base on reduction precluded our following analogous lines, namely:



It seemed possible, however, that at least a solution of the hydrochloride of *o*-benzoxyaniline might be obtained by preparing the benzylidene derivative of *o*-aminophenol, benzoylating this, and hydrolysing the product with dilute hydrochloric acid:



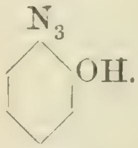
On attempting to benzoylate the benzylidene derivative of *o*-aminophenol, however, we found that alike in pyridine and in free alkali, benzaldehyde is eliminated, and the dibenzoyl derivative of *o*-aminophenol is produced; this change is the more curious when it is recalled that the benzylidene compound in question may be methylated in presence of sodium ethoxide, yielding the benzylidene compound of the corresponding anisidine (D.R.-P. 69006). The difficulty was ultimately overcome by selecting an acyl group which precluded anhydro-base formation, and by the use of *p*-toluenesulphonic chloride we were able to complete the connexion between *o*-nitrophenol and *o*-hydroxyphenylazoimide:



The derivative thus prepared is identical with the product obtained from *o*-hydroxyphenylazoimide and *p*-toluenesulphonic chloride.

EXPERIMENTAL.

o-*Hydroxyphenylazoimide*,



Forty grams of *o*-aminophenol hydrochloride in 300 c.c. of water mixed with 100 c.c. of concentrated hydrochloric acid were diazotised with 20 grams of sodium nitrite in 100 c.c. of water; to the well-iced liquid, 25 grams of hydroxylamine hydrochloride in 50 c.c. of water were added, the mixture being poured without delay into 1500 c.c. of ice-cold water in which 500 grams of crystallised sodium carbonate had been partly dissolved, sufficient water to dissolve all the salt rendering the bulk of liquid inconveniently great. The liberation of gas was inconsiderable, and the characteristic odour of *o*-hydroxyphenylazoimide soon became perceptible, but in order to complete the action the liquid was stirred continuously and maintained at zero during twelve hours, a slight accumulation of tar occurring. The filtered product, amounting to nearly 3 litres, was acidified with 100 c.c. of glacial acetic acid, some ether being first added to check frothing, and then extracted three times with 300 c.c. of ether. Although the ethereal solution was dark brown, it could be rendered almost colourless in successful experiments by agitation with 8 per cent. sodium carbonate solution, repeated 15—25 times, and on drying the faintly pink liquid with anhydrous sodium sulphate and stirring it vigorously with 60 c.c. of a 40 per cent. solution of sodium hydroxide, snow-white, lustrous crystals of the sodium derivative were obtained amounting to nearly 30 grams.

From this product the free phenol may be prepared by adding a deficit of mineral or acetic acid to the concentrated solution, there being produced an emulsion which quickly solidifies to brilliant, colourless needles; the slightest excess of acid, however, causes the product to liquefy, and in this condition it remains:

0·1460 gave 0·2659 CO_2 and 0·0570 H_2O. C = 49·86; H = 4·37.
0·2093 ,, 51·8 c.c. of nitrogen at 18° and 771 mm. N = 29·45.
$C_6H_5ON_3$ requires C = 53·33; H = 3·73; N = 31·11 per cent.
$2C_6H_5ON_3,H_2O$ requires C = 50·00; H = 4·16; N = 29·16 per cent.

The bimolecular structure of *o*-hydroxyphenylazoimide suggests an explanation of its behaviour towards acids, which probably resolve it into the unimolecular form. A determination of the molecular weight in phenol would appear to support this, an average value of 90 units being obtained; this agrees well with 96 units calculated from $\frac{1}{3}(2C_6H_5ON_3 + H_2O)$.

The substance has no definite melting point, becoming dark at 120—130°, and detonating vigorously at 140—145°, according to the rate at which the temperature is raised. It is moderately soluble in warm water, separating in long, lustrous, yellow needles as the liquid cools, and dissolves freely in alcohol, ethyl acetate, or acetone; in chloroform, petroleum, dry ether, or benzene, however, it is practically insoluble, and with the last-named it appears to form a compound, dissolving readily at first and quickly crystallising in felted needles, the water being displaced by the hydrocarbon. On attempting to recrystallise the compound by adding petroleum to a solution in ethyl acetate, a portion was obtained in faintly yellow, lustrous needles, but the greater part changed into tar, as the separation of crystals extended over a considerable period. Noticing that nitrobenzene is a fairly good solvent, we tried nitromethane, and found that this somewhat unusual medium is really most convenient, as it dissolves the hydroxyphenylazoimide only sparingly when cold, freely, however, on warming the liquid, which deposits beautiful, lustrous, yellow prisms.

The odour of the azoimide is very characteristic, recalling *o*-nitrophenol and *o*-salicylaldehyde in an intensified degree; the taste is intensely sweet and burning, with an after-taste recalling *o*-nitrophenol. It distils easily in steam, but quickly undergoes decomposition and cannot therefore be purified by this method. A crystal dropped in concentrated sulphuric acid detonates, producing a relatively large flame and a cloud of reddish-brown smoke; a solution in water, to which one drop of ammonia has been added, does not alter in appearance when treated with ammoniacal silver oxide, but on heating the liquid, oxidation takes place almost immediately, a silver mirror being produced. Ferric chloride in aqueous solution develops an intense blue coloration, which immediately becomes red, and this colour gradually disappears, giving place to a black precipitate. Nitrous acid converts the azoimide into a nitro-compound which crystallises from petroleum in long, lustrous, yellow needles, as in the case of the para-compound; it is volatile in steam, and soluble in water, forming a brick-red potassium derivative which crystallises in long needles, and is insoluble in excess of potash; the melting point of this nitro-compound is indefinite in the neighbourhood of 45°, but as the substance is very expensive to prepare, and is not of immediate interest, it has not been characterised further.

The Benzoyl Derivative.—When prepared by the Schotten-Baumann process the benzoyl derivative of *o*-hydroxyphenylazoimide is oily and solidifies with difficulty, but on cooling with ice a solution in warm petroleum (b. p. 50—60°) it separates in hard, lustrous plates, melting at 45°:

0·2132 gave 32·8 c.c. of nitrogen at 22° and 767 mm. N = 17·96.
$C_{13}H_9O_2N_3$ requires N = 17·57 per cent.

The substance is freely soluble in organic solvents, but does not dissolve in water.

The p-*Nitrobenzoyl Derivative.*—This compound crystallises from absolute alcohol in long, lustrous, faintly yellow prisms, and melts at 101°:

0·2126 gave 35·8 c.c. of nitrogen at 21° and 768 mm. N = 19·76.
$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is freely soluble in acetone or ethyl acetate, dissolving with great difficulty in benzene, and is insoluble in light petroleum.

The p-*Toluenesulphonic Derivative.*—On adding the calculated amount of *p*-toluenesulphonic chloride to the sodium derivative of *o*-hydroxyphenylazoimide in pyridine, the *p*-toluenesulphonic derivative is produced and crystallises from petroleum in lustrous, centimeter-long plates, which, with some difficulty, may be obtained colourless; it melts at 72°, and is freely soluble in chloroform and warm alcohol:

0·2020 gave 25·8 c.c. of nitrogen at 22° and 760 mm. N = 14·78.

$C_{13}H_{11}O_3N_3S$ requires N = 14·53 per cent.

With the object of obtaining *o*-hydroxyphenylazoimide by an independent method, we prepared the *p*-toluenesulphonic derivative indirectly from *o*-nitrophenol. The latter substance was converted into the *p*-toluenesulphonic derivative (Bamberger and Rising, *Ber.*, 1901, **34**, 241) and reduced under conditions somewhat more convenient than those described. Fifty grams were suspended in 300 c.c. of glacial acetic acid mixed with 60 c.c. of concentrated hydrochloric acid, 50 grams of tin foil being gradually added while the temperature was maintained below 40°; a further quantity of hydrochloric acid having been added, the liquid was stirred during one to two hours, filtered from undissolved metal, and poured into 2 litres of water containing 150 grams of sodium acetate. The precipitated base, which melted at 100—101° after crystallisation from alcohol, was diazotised in glacial acetic acid, mixed with hydrochloric acid, and treated with the necessary quantity of bromine dissolved in hydrobromic acid; the perbromide being oily was converted forthwith into the azoimide, which melted at 72°, and did not depress the melting point of a specimen prepared from *o*-hydroxyphenylazoimide and *p*-toluenesulphonic chloride. This process being a convenient one, it was hoped that by means of it the *o*-hydroxyphenylazoimide itself might be prepared from *o*-nitrophenol, but on attempting to hydrolyse the ester it was found that the *p*-toluenesulphonic group is so resistant as to preclude its removal under conditions which the azimidophenol is able to survive.

The Sodium Derivative.—The crude material obtained in the manner already indicated may be purified by dissolution in the minimum of hot absolute alcohol and mixing the filtered solution with four volumes of chloroform, which quickly precipitates long, lustrous, snow-white needles; ether cannot be used for this purpose in the place of chloroform, but the alcohol may be replaced by acetone or ethyl acetate:

0·1381 gave 24·6 c.c. of nitrogen at 20° and 765 mm. N = 20·69.
0·5216 „ 0·1806 Na_2SO_4. Na = 11·23.

$C_6H_4ON_3Na$ requires N = 26·75; Na = 14·65 per cent.

$C_6H_4ON_3Na,C_2H_6O$ requires N = 20·69; Na = 11·33 per cent.

Thus the sodium derivative of *o*-hydroxyphenylazoimide resembles the potassium derivative of the para-compound in crystallising with alcohol, but there the similarity terminates. When protected from light, it does not become green, although a yellow tinge is assumed; the colourless, aqueous solution certainly does evolve gas when heated, but the splendid blue colour associated with the *p*-hydroxyphenylazoimide is not developed, the liquid becoming brown with liberation of ammonia in traces, whilst an alcoholic solution is comparatively stable. A further distinction from the para-compound is noticed in the behaviour of an aqueous solution of the sodium derivative when boiled with excess of alkali. We have stated (*loc. cit.*, p. 857) that when an alcoholic solution of the colourless potassium derivative of *p*-hydroxyphenylazoimide is warmed with alcohol or water, it changes into the blue salt, and this, when boiled with water, yields two-thirds of its nitrogen content unaccompanied by hydrazoic acid; we now find that if the aqueous liquid is boiled with considerable excess of potash, hydrazoic acid, amounting roughly to 20 per cent., is liberated. On treating the ortho-compound in the same way, hydrazoic acid could not be detected, although 12 grams of the sodium salt were used at one time. This observation is the more interesting when it is recalled that, although in their behaviour towards alcoholic potash, ortho- and para-nitrophenylazoimides distinguish themselves from the meta-compound which does not yield hydrazoic acid, Noelting, Grandmougin, and Michel (*Ber.*, 1892, **25**, 3328) have shown that whilst the para-compound furnishes 40 per cent. of hydrazoic acid, only 10—15 per cent. is obtainable from *o*-nitrophenylazoimide.

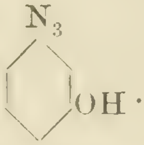
Like the free phenol, the sodium derivative has a sweet, burning taste, and when heated in a platinum dish, it explodes with considerable violence, the potassium derivative of the para-compound simply charring without explosion. When heated with hydroxylamine acetate in absolute alcohol, the sodium derivative does not undergo any definite change, and it is equally indifferent towards phenylhydrazine and semicarbazide; these experiments were made with the object of ascertaining whether the ortho-compound displayed any tendency to become transformed into a quinonoid variety.

The Potassium Derivative.—When concentrated aqueous potassium hydroxide is added to an aqueous solution of *o*-hydroxyphenylazoimide in the dilute alkali, long, silky needles are obtained; the substance is too readily soluble in water and in alcohol, however, to be purified without great difficulty, and as the sodium derivative could be investigated instead, the potassium compound was not studied further.

The Lead Derivative.—On mixing solutions of lead acetate and the sodium derivative of *o*-hydroxyphenylazoimide, the lead compound is precipitated. It is quite colourless, and practically insoluble, and in this respect resembles the lead derivative prepared from the colourless potassium compound of *p*-hydroxyphenylazoimide; we have not noticed a blue lead salt corresponding with the one precipitated on adding lead acetate to an aqueous solution of the blue potassium derivative of *p*-hydroxyphenylazoimide, which is also deep blue and which, nevertheless, yields with methyl iodide the methyl ether obtained from the perbromide of diazotised *p*-anisidine and ammonia.

The Silver Derivative.—This compound is obtained as a pale yellow, curdy precipitate on adding silver nitrate to an aqueous solution of the sodium compound; even when a deficit of silver nitrate is used, however, the substance becomes black in a few seconds.

m-*Hydroxyphenylazoimide*,



In preparing this compound it was found necessary to depart from previous practice by using great excess of hydroxylamine. Twenty grams of *m*-aminophenol were dissolved in 100 c.c. of concentrated hydrochloric acid, mixed with 100 c.c. of water, and diazotised with 13 grams of sodium nitrite; 70 grams of hydroxylamine hydrochloride in 200 c.c. of water were then added, and the mixture poured very slowly into 2 litres of ice-water containing 300 grams of anhydrous sodium carbonate. A red precipitate was produced immediately, and in a few seconds the characteristic odour of *m*-hydroxyphenylazoimide became perceptible. After maintaining the temperature of the well-stirred liquid below zero during four hours, the colour had become orange and the phenol was then removed by agitating three times with 300 c.c. of ether, the combined extracts being purified by 5 per cent. sodium carbonate, which continued to dissolve a coloured by-product after twenty-five extractions. Having dried the pale yellow ethereal solution with calcium chloride and evaporated the solvent, an oil remained, which, when dried in the desiccator, solidified immediately in a freezing mixture, but liquefied again when the temperature rose to that of the laboratory. A pure specimen was obtained, however, by converting this material into the benzoyl derivative, hydrolysing the latter with alcoholic hydrochloric acid, and evaporating an ethereal extract which had been shaken well with sodium carbonate and dried with sodium sulphate. The oil obtained in this manner solidified when cooled, and the solid could be drained on porous earthenware; it was then extracted with warm petroleum (b. p. 50—60°), which deposited long, lustrous, colourless needles, melting at 36·5°, and quickly becoming brown on exposure to light:

0·1368 gave 37·0 c.c. of nitrogen at 22° and 760 mm. N = 31·29.
$C_6H_5ON_3$ requires N = 31·11 per cent.

The substance is very readily soluble in all organic media excepting cold petroleum; when mixed with water, it behaves like ordinary phenol, becoming oily, and then dissolving. It has a most characteristic odour which recalls that of β-naphthol, being at the same time sweet and pungent; the taste also is intensely sweet, quite devoid of after-taste, resembling sucrose. When dropped into concentrated sulphuric acid there is vigorous and instantaneous decomposition. *m*-Hydroxyphenylazoimide does not reduce an ammoniacal solution of silver oxide even when boiled for some minutes with the reagent; ferric chloride in aqueous solution develops a beautiful, violet coloration, which persists during several hours. The alkali derivatives furnish a marked distinction from those of the isomerides, being readily soluble in excess of alkali hydroxide and undergoing no colour change when the aqueous solution is boiled. A colourless, insoluble lead salt is precipitated when the phenol, dissolved in dilute ammonia, is treated with an ammonical solution of lead acetate.

The Benzoyl Derivative.—This compound was prepared as an intermediate stage in the purification of the phenol, and after crystallisation from boiling petroleum, formed lustrous, faintly yellow needles, melting at 50° without decomposition:

0·2344 gave 35·6 c.c. of nitrogen at 22° and 760 mm. N = 17·62.
$C_{13}H_9O_2N_3$ requires N = 17·57 per cent.

It dissolves readily in alcohol, acetone, or warm petroleum. Light turns it dark yellow, and concentrated sulphuric acid decomposes it vigorously.

The p-*Nitrobenzoyl Derivative.*—The Schotten-Baumann method is more convenient than pyridine for the preparation of this substance, which crystallises from benzene in amber-yellow, hard, irregular cubes, melting at 136° without decomposition:

0·1768 gave 30·0 c.c. of nitrogen at 23° and 763 mm. N = 19·71.
$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is moderately soluble in acetone and benzene, but dissolves sparingly in boiling alcohol; with concentrated sulphuric acid it decomposes vigorously.

The p-*Nitrobenzoyl Derivative of* p-*Hydroxyphenylazoimide.*

For the purpose of comparison, as indicated above, this compound was prepared from *p*-nitrobenzoyl chloride and an alkaline solution of the phenol, and crystallised from acetone in long, lustrous, pale yellow needles, which melt and decompose at 169—170°:

0·1118 gave 19·4 c.c. of nitrogen at 22° and 760 mm. N = 20·08.

$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is very sparingly soluble in hot alcohol or benzene, and decomposes immediately with concentrated sulphuric acid.

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CXXV.—*Methyl Dicarboxyaconitate.*

By SIEGFRIED RUHEMANN.

THE observation that ethyl dicarboxyglutaconate, on treatment with ammonia, decomposes according to the equation

$$(CO_2Et)_2C{:}CH{\cdot}CH(CO_2Et)_2 + 3NH_3 = CH_2{\cdot}(CO{\cdot}NH_2)_2 + NH_2{\cdot}CH{:}C(CO_2Et)_2{}^* + 2C_6H_5{\cdot}OH$$

(Ruhemann and Morrell, Trans., 1891, **69**, 743) has been the starting point of a series of experiments on the reaction between the ester and primary and secondary organic bases. In several later papers it has been shown that those bases behave towards the ester in a manner similar to ammonia and yield alkyl and aryl derivatives of ethyl aminomethylenemalonate, which in certain cases condense to heterocyclic compounds. In this way the synthesis of 5-pyrazolone and several of its derivatives, as well as the formation of substances belonging to the pyrimidine series, has been effected.

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* I take this opportunity of mentioning that I studied, some time ago, the action of potassium cyanate on ethyl aminomethylenemalonate, and obtained ethyl uramidomethylenemalonate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH{:}C(CO_2Et)_2$, which Wheeler, Johnson, and Johns (*Amer. Chem. Journ.*, 1907, **37**, 392) recently detected as a by-product in the condensation of ethyl ethoxymethylenemalonate with ethyl-ψ-thiocarbamide hydrobromide. I have prepared the compound by mixing the solution of ethyl aminomethylenemalonate (3 grams) in about 70 c.c. of hot water with potassium cyanate (3 grams), dissolved in a little water, and digesting the mixture on the water-bath for an hour. On adding hydrochloric acid to the cold solution, a solid separates in the course of two days. This is readily soluble in hot alcohol, sparingly so, however, in boiling water, and, on cooling, crystallises in colourless plates which melt at 205° with evolution of gas:

0·2010 gave 0·3450 CO_2 and 0·1112 H_2O. C = 46·81; H = 6·14.
0·2220 ,, 23·4 c.c. moist nitrogen at 17° and 762 mm. N = 12·26.
$C_9H_{14}O_5N_2$ requires C = 46·95; H = 6·09; N = 12·17 per cent.

I had intended to study this ester in a similar manner to that used by the above named chemists, but I have been unable to do so owing to the small yield of the compound which I have obtained.

The fact that ethyl dicarboxyglutaconate, under the influence of ammonia and organic bases, decomposes in the manner indicated by the above equation, and that the disruption of the ester takes place at the single carbon-linking, has led to a closer investigation of the reaction. Guthzeit (*Ber.*, 1897, **30**, 1757) has found that the ester forms with aniline an additive product, ethyl anilinodicarboxyglutarate, which, however, is unstable, and readily decomposes into ethyl anilinomethylenemalonate and ethyl malonate:

$$C_6H_5{\cdot}NH{\cdot}CH[CH(CO_2Et)_2]_2 = C_6H_5{\cdot}NH{\cdot}CH\colon C(CO_2Et)_2 + CH_2(CO_2Et)_2.$$

This experiment tends to show that the disruption of ethyl dicarboxyglutaconate is preceded by the formation of additive compounds of the ester with bases. This conclusion is supported by the results which the study of the behaviour of organic bases towards unsaturated compounds has furnished. Ruhemann and Browning (Trans., 1898, **73**, 723) have shown that piperidine readily unites with esters of olefinic acids, such as fumaric, citraconic, and aconitic acids. These, however, are very stable; they can be distilled under diminished pressure, and form stable hydrochlorides. We have stated, also, that the ester of the acetylenic acid, ethyl phenylpropiolate, unites with piperidine to yield ethyl phenylpiperidylcinnamate. This, as has been pointed out, behaves differently from the corresponding compounds which are formed from the esters of olefinic acids, as it reacts with hydrogen chloride to yield a pasty product. We had assumed (*loc. cit.*) that this was the hydrochloride of the additive product, but Moureu and Lazennec (*Compt. rend.*, 1906, **143**, 596) have shown recently that the products of the union of organic bases with ethyl phenylpropiolate, as well as the esters of other acetylenic acids, on treatment with hydrogen chloride yield the hydrochlorides of the bases and β-ketonic esters.

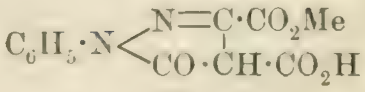
Different, however, is the behaviour of organic bases towards olefinic ketonic compounds. Ruhemann and Watson (Trans., 1904, **85**, 466, 1170) have shown that in this case additive products are formed; benzylideneacetylacetone, for instance, unites with aniline, but the substance which is produced, on heating at 100°, decomposes into benzylideneaniline and acetylacetone, thus:

$$C_6H_5{\cdot}CH(NH{\cdot}C_6H_5){\cdot}CH(CO{\cdot}CH_3)_2 = C_6H_5{\cdot}CH\colon N{\cdot}C_6H_5 + CH_2(CO{\cdot}CH_3)_2.$$

These reactions closely resemble the decomposition which ethyl dicarboxyglutaconate undergoes on treatment with ammonia or organic bases.

The results of this work on ethyl dicarboxyglutaconate induced me to examine whether compounds in which the hydrogen of chloroform is replaced by hydrocarbon or acid groups would react with ethyl sodiomalonate in the same way as chloroform. The substances which were supposed to be formed might be expected to behave towards bases in a similar manner as ethyl dicarboxyglutaconate. Experiments in this direction, which were undertaken some time ago, were unsuccessful, because, as has been stated (*Ber.*, 1896, **29**, 1016), *ααα*-trichloroethane has no action on the sodium derivative of ethyl malonate, nor, as I have found since, does benzotrichloride react with it. Ethyl trichloroacetate, as I have also shown (*loc. cit.*), on treatment with a mixture of alcoholic sodium ethoxide and ethyl malonate, does not yield ethyl dicarboxyaconitate. This result, most probably, is due to the decomposition of ethyl trichloroacetate and the action of the resulting chloroform on the malonic ester. With the object of proving the correctness of this view I have now repeated the experiment, using, however, the sodium derivative of methyl malonate, which was prepared by the action of metallic sodium on the solution of the ester in absolute ether, but hardly any change takes place on digesting it with methyl trichloroacetate for several days. Methyl dicarboxyaconitate, $(CO_2Me)_2CH\cdot C(CO_2Me):C(CO_2Me)_2$, as Anschütz (*Annalen*, 1903, **327**, 233) has shown, is formed by the action of the dimethyl ester of dichloroglycollic acid (methyl dichloro-oxalate) on methyl sodiomalonate, suspended in dry ether. I have prepared this ester according to the directions of Anschütz and Deschauer (*Annalen*, 1906, **347**, 3) in order to study it in a similar manner to ethyl dicarboxyglutaconate. This investigation has led to the following results.

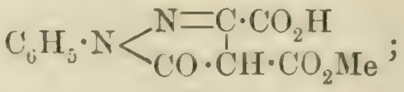
Phenylhydrazine reacts with the solution of the ester in dry ether to yield an additive product. The fact that this is colourless points to the formula $CO_2Me\cdot C(NH\cdot NH\cdot C_6H_5)[CH(CO_2Me)_2]_2$, according to which it is to be regarded as methyl phenylhydrazinodicarboxytricarballylate. The compound is fairly stable, and in this respect differs from the corresponding substance which may be supposed to be, first, formed from ethyl dicarboxyglutaconate and phenylhydrazine. Whilst the latter product decomposes in the course of the reaction to furnish ethyl malonate and ethyl 1-phenyl-5-pyrazolone-4-carboxylate, the additive compound of the hydrazine with methyl dicarboxyaconitate does not suffer a similar change until it is digested with dilute aqueous potassium hydroxide or boiled with sodium carbonate. Dimethyl 1-phenyl-5-pyrazolone-3-4-dicarboxylate, which undoubtedly is first formed along with malonic acid, is, however, partially hydrolysed, and yields the monomethyl ester of the pyrazolonedicarboxylic acid. This, a priori, may be expressed either by the formula



$$\mathrm{C_6H_5\cdot N}\Big<\begin{matrix}\mathrm{N{=}C\cdot CO_2Me}\\ \mathrm{CO\cdot CH\cdot CO_2H}\end{matrix}$$

(I.)

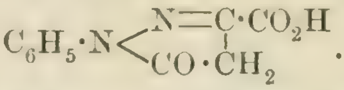
or



$$\mathrm{C_6H_5\cdot N}\Big<\begin{matrix}\mathrm{N{=}C\cdot CO_2H}\\ \mathrm{CO\cdot CH\cdot CO_2Me}\end{matrix};$$

(II.)

the fact, however, that 5-pyrazolone-4-carboxylic acid and its 1-phenyl derivative are very unstable and lose carbon dioxide below 100°, whereas the substance which is formed from methyl dicarboxyaconitate melts and decomposes at 200°, points to formula (I). The hydrolysis of this compound, which is effected by boiling it with concentrated aqueous potassium hydroxide, is accompanied by the loss of carbon dioxide, and yields 1-phenyl-5-pyrazolone-3-carboxylic acid,

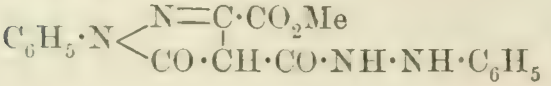


$$\mathrm{C_6H_5\cdot N}\Big<\begin{matrix}\mathrm{N{=}C\cdot CO_2H}\\ \mathrm{CO\cdot CH_2}\end{matrix}.$$

Different from the behaviour of phenylhydrazine towards methyl dicarboxyaconitate at the ordinary temperature, is the interaction of the two substances at 100°. The ester decomposes and yields methyl malonate besides a colourless compound having the formula $C_{24}H_{24}O_4N_6$. This is characterised as a phenylhydrazine salt, because its solution reacts with hydrochloric acid, thus:

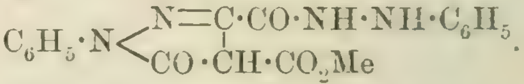
$$C_{24}H_{24}O_4N_6 + HCl = C_6H_5NH\cdot NH_2,HCl + C_{18}H_{16}O_4N_4.$$

The product $C_{18}H_{16}O_4N_4$ on treatment with sodium carbonate readily loses phenylhydrazine; it is therefore to be regarded as the phenylhydrazide of monomethyl phenylpyrazolonedicarboxylate. With regard to its constitution there remains the choice between the formulæ



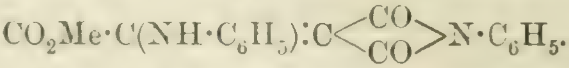
$$\mathrm{C_6H_5\cdot N}\Big<\begin{matrix}\mathrm{N{=}C\cdot CO_2Me}\\ \mathrm{CO\cdot CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5}\end{matrix}$$

and



$$\mathrm{C_6H_5\cdot N}\Big<\begin{matrix}\mathrm{N{=}C\cdot CO\cdot NH\cdot NH\cdot C_6H_5}\\ \mathrm{CO\cdot CH\cdot CO_2Me}\end{matrix}.$$

Aniline, like phenylhydrazine, decomposes methyl dicarboxyaconitate if the mixture of the two reagents is heated on the water-bath. The ester, $CO_2Me\cdot C(NH\cdot C_6H_5):C(CO_2Me)_2$, which, besides methyl malonate, may be expected to be produced, does not make its appearance, but is transformed into methyl carboxyanilinomethylenemalonanil,



$$\mathrm{CO_2Me\cdot C(NH\cdot C_6H_5){:}C}\Big<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\Big>\mathrm{N\cdot C_6H_5}.$$

The behaviour of methyl dicarboxyaconitate towards ammonia and hydroxylamine is still under examination, and will form the subject of a subsequent communication.

EXPERIMENTAL.

Action of Phenylhydrazine on Methyl Dicarboxyaconitate at the Ordinary Temperature.

Methyl Phenylhydrazinodicarboxytricarballylate, $CH_3\cdot CO_2\cdot C(NH\cdot NH\cdot C_6H_5)[CH(CO_2\cdot CH_3)_2]_2$.

This compound is readily formed on adding phenylhydrazine to methyl dicarboxyaconitate dissolved in dry ether. In the course of a few hours, beautiful colourless prisms separate which, on standing overnight, increase in quantity; the yield is more than 90 per cent. of the theoretical.

The substance after being washed with ether melts at 135°:

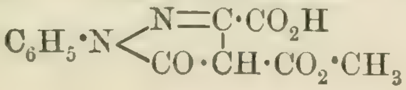
0·2005 gave 0·3795 CO_2 and 0·1000 H_2O. C = 51·62; H = 5·54.
0·2260 „ 12·4 c.c. moist nitrogen at 17° and 779 mm. N = 6·52.
$C_{19}H_{24}O_{10}N_2$ requires C = 51·81; H = 5·45; N = 6·36 per cent.

Dilute alkali hydroxides or carbonates decompose the additive product, thus:

$$C_{19}H_{24}O_{10}N_2 + 3H_2O = C_{12}H_{10}O_5N_2 + CH_2(CO_2H)_2 + 4CH_3\cdot OH,$$

and yield

4-*Monomethyl* 1-*Phenyl*-5-*pyrazolone*-3-4-*dicarboxylate*,



$$C_6H_5\cdot N\left<\begin{array}{l} N{=}C\cdot CO_2H \\ CO\cdot \overset{|}{C}H\cdot CO_2\cdot CH_3 \end{array}\right.$$

On using dilute aqueous potassium hydroxide, the compound $C_{19}H_{24}O_{10}N_2$ dissolves after short digestion, and the yellow solution which is formed gives with hydrochloric acid a white precipitate. This crystallises from dilute alcohol in colourless prisms which soften at 195° and melt at 201—202° with evolution of gas:

0·2024 gave 0·4085 CO_2 and 0·0735 H_2O. C = 55·04; H = 4·03.
0·1671 „ 0·3360 CO_2 and 0·0585 H_2O. C = 54·83; H = 3·88.
0·2470 „ 22·5 c.c. moist nitrogen at 14° and 763 mm. N = 10·76.
$C_{12}H_{10}O_5N_2$ requires C = 54·96; H = 3·81; N = 10·69 per cent.

The pyrazolone derivative is only sparingly soluble in boiling water, but dissolves readily in alcohol, and the alcoholic solution gives a deep red coloration with ferric chloride; it dissolves with great ease in sodium carbonate or ammonia, and the ammoniacal solution yields with silver nitrate a gelatinous, white precipitate which, on boiling, becomes curdy.

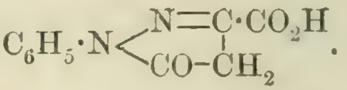
The same decomposition of the additive product takes place on heating it with sodium carbonate; after about an hour's boiling, the whole is dissolved, and the yellow solution, on treatment with hydrochloric acid, furnishes monomethyl phenylpyrazolonedicarboxylate. The filtrate from this compound contains malonic acid. It was isolated by evaporating the acid solution to dryness, extracting the residue with ether, decolorising the ethereal solution by means of animal charcoal, and distilling off the ether. The solid which is left behind was identified as malonic acid by the melting point (131—132°) and the following analysis:

0·1717 gave 0·2185 CO_2 and 0·0610 H_2O. C = 34·70; H = 3·94.

$C_3H_4O_4$ requires C = 34·61; H = 3·84 per cent.

On boiling monomethyl phenylpyrazolonedicarboxylate with concentrated aqueous potassium hydroxide (50 per cent.) for an hour, hydrolysis, accompanied by the loss of carbon dioxide, takes place, and there is formed

1-*Phenyl*-5-*pyrazolone*-3-*carboxylic Acid*,



$$C_6H_5\cdot N\begin{cases}N{=}C\cdot CO_2H \\ CO{-}CH_2\end{cases}.$$

This substance is precipitated as a white solid on adding hydrochloric acid to the alkaline solution. It dissolves readily in alcohol, but only sparingly in boiling water, and crystallises from either solution in colourless needles which melt at about 261° with evolution of gas. The identity of this substance with the known 1-phenyl-5-pyrazolone-3-carboxylic acid was verified by the following analysis:

0·1615 gave 0·3488 CO_2 and 0·0593 H_2O. C = 58·90; H = 4·07.

0·1736 ,, 20·4 c.c. moist nitrogen at 15° and 759 mm. N = 13·74.

$C_{10}H_8O_3N_2$ requires C = 58·82; H = 3·92; N = 13·72 per cent.

Action of Phenylhydrazine on Methyl Dicarboxyaconitate at 100°.

On heating equal weights of phenylhydrazine and methyl dicarboxyaconitate on the water-bath for an hour, the whole sets to a semi-solid. This is washed with methyl alcohol, when a colourless substance is left behind which melts at 224° with evolution of gas and turns yellow in the course of a week:

0·1990 gave 0·4558 CO_2 and 0·0953 H_2O. C = 62·47; H = 5·32.

0·1705 ,, 27·2 c.c. moist nitrogen at 15° and 744 mm. N = 18·28.

$C_{24}H_{24}O_4N_6$ requires C = 62·62; H = 5·21; N = 18·26 per cent.

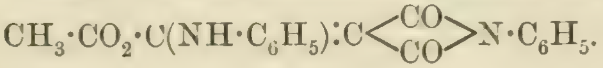
This substance, as has been pointed out (p. 1362), is a phenylhydrazine salt. As such it is characterised by the fact that its solution in dilute alcohol, on treatment with hydrochloric acid, yields phenylhydrazine hydrochloride; at the same time a precipitate is formed, which is the *phenylhydrazide* of *monomethyl phenylpyrazolonedicarboxylate*. Its constitution is to be represented by one of the two formulæ given before (*loc. cit.*). The compound is sparingly soluble in cold, but readily in boiling alcohol, and, on cooling, crystallises in clusters of colourless, curved needles which, when heated, darken, but do not melt, above 250°:

0·2016 gave 0·4520 CO_2 and 0·0863 H_2O. C = 61·14; H = 4·75.
0·2262 „ 30·0 c.c. moist nitrogen at 15° and 779 mm. N = 15·92.
$C_{18}H_{16}O_4N_4$ requires C = 61·36; H = 4·54; N = 15·91 per cent.

The phenylhydrazide develops the odour of phenylhydrazine when agitated with cold sodium carbonate.

Action of Aniline on Methyl Dicarboxyaconitate.

Methyl Carboxyanilinomethylenemalonanil,



$$CH_3\cdot CO_2\cdot C(NH\cdot C_6H_5){:}C{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N\cdot C_6H_5.$$

A mixture of equal weights of aniline and methyl dicarboxyaconitate, when heated on the water-bath for two to three hours, yields a red oil from which, on being kept overnight, a yellow solid separates. This gradually crystallises from its solution in methyl alcohol in canary-yellow prisms which melt at 194°:

0·1820 gave 0·4471 CO_2 and 0·0730 H_2O. C = 67·0; H = 4·45.
0·1696 „ 12·9 c.c. moist nitrogen at 18° and 753 mm. N = 8·77.
$C_{18}H_{14}O_4N_2$ requires C = 67·08; H = 4·35; N = 8·69 per cent.

This compound is somewhat soluble in cold alcohol, benzene, or chloroform, but dissolves readily in the boiling solvents.

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CXXVI.—*The Action of Heat on α-Hydroxycarboxylic Acids. Part III. αα′-Dihydroxysebacic Acid and its Diacetyl Derivative.*

By HENRY RONDEL LE SUEUR.

THE previous communications (Trans., 1904, **85**, 827; 1905, **87**, 1888) relating to this investigation dealt with the α-monohydroxy-derivatives of monocarboxylic acids, and it was shown that when these acids are heated at 270° they decompose with evolution of carbon monoxide and formation of aldehydes containing one atom of carbon less than the parent hydroxy-acids

$$R\cdot CH(OH)\cdot CO_2H \longrightarrow R\cdot CHO + CO + H_2O.$$

The present communication deals with a similar investigation of the action of heat on $\alpha\alpha'$-dihydroxysebacic acid and its diacetyl derivative, and the results now brought forward show that these compounds when heated undergo a decomposition similar to that of the monohydroxy-derivatives of the monobasic acids:

$$CO_2H{\cdot}CH(OH){\cdot}[CH_2]_6{\cdot}CH(OH){\cdot}CO_2H \longrightarrow CHO{\cdot}[CH_2]_6{\cdot}CHO + CO + H_2O.$$

$$CO_2H{\cdot}CH(OAc){\cdot}[CH_2]_6{\cdot}CH(OAc){\cdot}CO_2H \longrightarrow CHO{\cdot}[CH_2]_6{\cdot}CHO + CH_3{\cdot}CO_2H + CO.$$

In this case the aldehyde produced is suberic dialdehyde, a substance which has been obtained previously by Baeyer (*Ber.*, 1897, **30**, 1962) by the oxidation of the barium salt of dihydroxysebacic acid by means of lead dioxide and phosphoric acid. Baeyer showed that this dialdehyde is a liquid which very readily polymerises, and that even after the short interval of half an hour the substance has polymerised to a caoutchouc-like mass.

The present author was unable to obtain the aldehyde in a pure state, a want of success which in his opinion is to be ascribed to the unstable nature of the aldehyde rather than to the inapplicability of this method to the α-hydroxy-derivatives of dibasic acids in general.

That suberic dialdehyde is produced by heating $\alpha\alpha$-dihydroxysebacic acid or its diacetyl derivative is proved conclusively by the fact that the product obtained polymerised as described by Baeyer, that it formed a crystalline compound with sodium hydrogen sulphite, and when oxidised with potassium permanganate gave suberic acid; further, it formed an oxime which melted at the same temperature as the oxime of suberic dialdehyde.

It was intended to include in this communication the investigation of the action of heat on α-monohydroxysebacic acid, which it was hoped to obtain by the hydrolysis of the corresponding α-monobromo-derivative. Unfortunately all attempts to prepare this bromo-derivative have failed up to the present, and in all cases where this substance might be expected to be produced only the dibromo-derivative or unbrominated sebacic acid was obtained, and there was no satisfactory evidence of the formation of the monobromo-derivative.

The following is a very brief summary of some of the experiments made in this direction:

(*a*) Bromination of sebacic acid with amorphous phosphorus and bromine, using only sufficient bromine to form the monobromo-derivative of the acid dibromide.

(*b*) Conversion of the sebacic acid (1 mol.) into its acid chloride by means of phosphorus pentachloride, and acting on the resulting compound with bromine (1 mol.).

(*c*) The interaction of equimolecular proportions of bromine and the mono-acid chloride of the monoethyl ester of sebacic acid.

EXPERIMENTAL.

Preparation of $\alpha\alpha'$-Dibromosebacic Acid.

Forty grams of dry bromine were gradually added to an intimate mixture of 1·5 grams of dry amorphous phosphorus and 12 grams of sebacic acid (m. p. 130—131°), and the whole heated on the water-bath for five hours, at the end of which time the whole of the free bromine had disappeared. The resulting bromo-acid bromide was gradually poured into 40 c.c. of formic acid (sp. gr. 1·22) and the whole heated on the water-bath for half an hour. The dibromo-acid which separated after cooling was filtered and recrystallised, first from formic acid and then finally from chloroform until its melting point was constant:

0·2554 gave 0·2663 AgBr. Br = 44·36.
$C_{10}H_{16}O_4Br_2$ requires Br = 44·44 per cent.

$\alpha\alpha'$-Dibromosebacic acid crystallises in long needles melting at 117—120°. The melting point found for this substance by Auwers and Bernhardi (*Ber.*, 1891, **24**, 2232) is 117·5—119°, whereas Weger (*Ber.*, 1894, **27**, 1212) states that it melts at 136°, and Claus and Steinkauler (*Ber.*, 1887, **20**, 2883) quote 115° as the melting point of the pure substance.

Preparation of $\alpha\alpha'$-Dihydroxysebacic Acid.

Ten grams of the pure $\alpha\alpha'$-dibromosebacic acid were neutralised with 50 c.c. of an aqueous solution of sodium hydroxide and the solution of the sodium salt boiled for one and a half hours. The resulting strongly acid solution was again neutralised with sodium hydroxide and boiled for another hour, and this process repeated until the solution no longer became acid after boiling for a period of one hour. The resulting dihydroxy-acid was converted into the insoluble zinc salt, which, after being washed free from sodium bromide, was decomposed with hydrogen sulphide. The aqueous solution of the free acid was filtered from the zinc sulphide, evaporated to dryness, and the acid recrystallised from a mixture of ethyl acetate and chloroform, when it melted at 125—127°:

0·1534 gave 0·2888 CO_2 and 0·1088 H_2O. C = 51·34; H = 7·88.
$C_{10}H_{18}O_6$ requires C = 51·28; H = 7·69 per cent.

Claus and Steinkauler (*loc. cit.*, 2888) quote 130° as the melting point of this acid, whereas Weber (*loc. cit.*, 1215) states that it melts at 124°.

Action of Heat on αα′-Dihydroxysebacic Acid.

The pure dihydroxysebacic acid was heated in a distillation flask attached to a condenser; when the temperature reached 230° the substance frothed a good deal, carbon monoxide was evolved, and a small quantity of liquid distilled over. As the temperature rose, the mass gradually turned yellow and showed signs of charring, and although the temperature was raised to above 300°, very little more liquid distilled. The small quantity of distillate which was obtained had a characteristic odour of œnanthaldehyde, readily reduced potassium permanganate, and formed a semicarbazone melting at 176—181° and decomposing with evolution of gas at 184°.

Baeyer (*Ber.*, 1897, **30**, 1964) states that the semicarbazone of suberic dialdehyde melts and evolves gas at 183—185°.

The above experiment shows that suberic dialdehyde is formed when αα′-dihydroxysebacic acid is heated, but as the yield was very small, it was decided to try the action of heat on the diacetyl derivative of the acid, and this experiment was attended with more satisfactory results.

Action of Heat on the Diacetyl Derivative of αα′-Dihydroxysebacic Acid.

Preparation of the Diacetyl Derivative.—Forty grams of dihydroxysebacic acid, 80 grams of fused sodium acetate, and 320 grams of acetic anhydride were mixed together in a flask attached to a reflux condenser, and the mixture boiled for five and a half hours. The excess of acetic anhydride was removed by distillation in a vacuum and the residue dissolved in water; on the addition of an excess of dilute sulphuric acid to this solution, the acetyl derivative was precipitated as an oil, which was extracted with ether, and the ethereal solution washed, dried, and evaporated.

The *diacetyl derivative of αα′-dihydroxysebacic acid*,

$$CO_2H\cdot CH(OAc)\cdot[CH_2]_6\cdot CH(OAc)\cdot CO_2H,$$

is a thick oil which is insoluble in water and does not solidify on keeping for a long time or on cooling to a low temperature; as it cannot be distilled even in a vacuum without decomposition, it was not further purified.

Fifty grams of the diacetyl derivative were heated in a distillation flask attached to a condenser and provided with a thermometer whicl dipped into the substance. When the temperature reached 210° colourless liquid, chiefly acetic acid, distilled over; at 230° the ma frothed and carbon monoxide was evolved, and at 250° the evolution of gas was rapid, and an oily, yellow liquid passed over. When the temperature reached 300° the heating was discontinued as the evolution of carbon monoxide had practically ceased, and there was evidence of a secondary decomposition. The residue left in the flask was of a very spongy nature, and weighed 5 grams. The carbon monoxide was collected, and its volume corresponded approximately with that required by theory; it contained a small percentage of carbon dioxide. The distillate obtained from the heating of three quantities of 50 grams each was dried over anhydrous sodium sulphate and then distilled in air until the temperature had reached 140°, when the distillation was continued in a vacuum. After repeated distillation, a fraction boiling at 143—148°, under 33 mm. pressure, was obtained, which had the characteristic properties of the dialdehyde of suberic acid. It had a characteristic odour of œnanthaldehyde, polymerised to a semi-transparent yellow solid, formed a crystalline compound with sodium hydrogen sulphite, and readily reduced potassium permanganate in the cold.

A portion of the above fraction was dissolved in acetone and finely-powdered potassium permanganate added until no further reduction took place on heating. The residue left after evaporation of the acetone was diluted with water and acidified with dilute sulphuric acid, and the manganese dioxide dissolved by means of sulphurous acid. The resulting liquid was repeatedly extracted with ether, and the residue left on evaporation of the ethereal solution was crystallised first from ether and lastly from water, when it melted at 139—140°, which is the melting point of suberic acid. It was analysed with the following result:

0·1476 gave 0·2972 CO_2 and 0·1096 H_2O. $C = 54·91$; $H = 8·25$.

$C_8H_{14}O_4$ requires $C = 55·17$; $H = 8·05$ per cent.

Another portion of the same fraction was treated with hydroxylamine hydrochloride and sodium acetate in the usual way, and the oxime, which separated after some time, was recrystallised from absolute alcohol, when it melted at 151—152°, a melting point which agrees with that given by Baeyer (*loc. cit.*) for the dioxime of suberic dialdehyde, namely, 150—155°. On analysis:

0·1222 gave 16·7 c.c. moist nitrogen at 16° and 764 mm. $N = 16·02$.

$C_8H_{16}O_2N_2$ requires $N = 16·27$ per cent.

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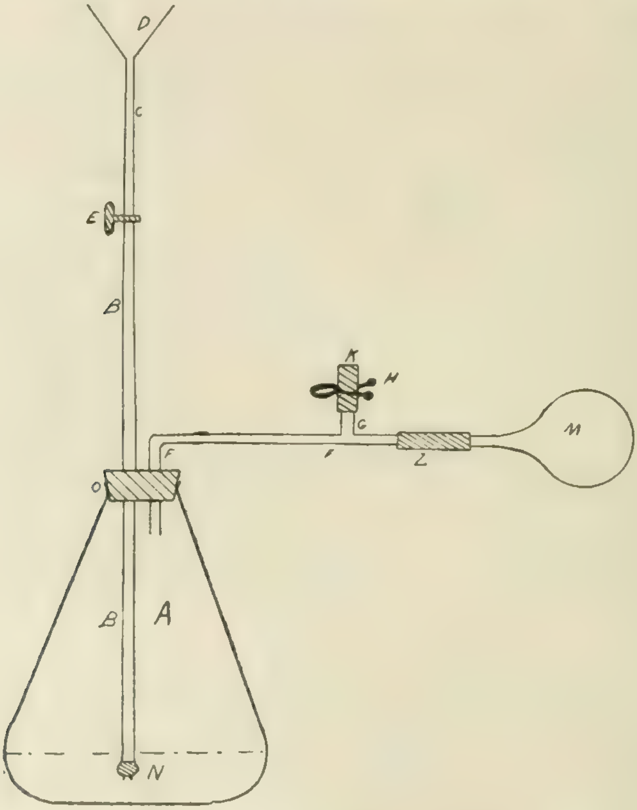
CXXVII.—*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*

By William Robert Lang and Thos. Boles Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) describe an apparatus for the rapid and exact estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in narrow tubes. (For a short description of their apparatus see Abstr., 1906, **90**, ii, 627.) The authors have modified this apparatus materially; the following short description and diagram will serve to explain it.



The vessel, *A*, containing the acidified sulphate is placed on a flat burner, the approximate amount of barium chloride solution, ascertained by previous rough experiments, run directly into the flask, the stopper, *O*, with its attachments, inserted, and the contents kept at the boiling point. *FF* is a T-tube, on the branch, *G*, of which is fixed a small piece of rubber tubing with a pinchcock, at this stage of the experiment left open to the air. *N* is a small thistle-shaped tube filled with glass-wool which is found materially to clear the turbid solution as it passes up to the narrow tube. The pinchcock, *H*, is then closed and a slight pressure on *M* forces a portion of the contents of the flask through *N* and up *B* until the portion *C* is filled, when the stopcock, *E*, is closed. The whole pressure on the flask can then be relieved by opening the pinchcock, *H*. The liquid in *C* clears very rapidly and the standard barium chloride solution may be added. If this produces a turbidity, *E* is opened and the solution washed down into the flask ; a very complete mixing is then obtained by alternately compressing *M*, with *G* open to the air, placing the finger on the orifice of the short rubber tube, *K*, and releasing *M*, thus causing air to be drawn through *N* and to bubble through the solution.

The process of forcing the liquid up the tube, titrating, washing it down again, and mixing is repeated until a further addition of barium chloride solution causes no turbidity. The mean between the number of c.c. used up to the point of having an evident turbidity and the quantity necessary to the point where none is perceptible is taken as the amount of barium chloride solution consumed in the precipitation of the sulphate. As the amounts of barium salt and sulphate in solution approximate to each other, so the rapidity of the clearing increases, and when the reaction has almost reached the end-point this clarification is very nearly instantaneous.

Experiments were undertaken in this apparatus with the solutions of sulphates and barium salts given in the following tables :

TABLE I.

Using 0·0958*N* – H_2SO_4, 1 c.c. = 0·0046 gram (SO_4).
,, 0·1101 *N* – $Ba(NO_3)_2$, 1 ,, = 0·00485 ,, (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
10·42	0·0479	10·00	0·0485	–1·0
10·60	0·0488	10·00	0·0435	+0·6
10·52	0·0484	10·00	0·0485	–0·2
10·58	0·0487	10·00	0·0485	+0·4
16·80	0·0773	16·00	0·0776	–0·3
15·71	0·0722	15·00	0·0727	–0·7

Average error –0·55 and +0·5, giving a mean error of 0·025 per cent.

TABLE II.

Using 0·9981 *N* – H_2SO_4, 1 c.c. = 0·0479 gram (SO_4).
,, 0·1101 *N* – $Ba(NO_3)_2$, 1 ,, = 0·00485 ,, (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
5·05	0·2419	50·00	0·2425	0·4
5·08	0·2433	50·00	0·2425	0·4
5·09	0·2438	50·00	0·2428	0·5

Average error............ 0·43

TABLE III.

Using 0·2039 N – H_2SO_4, 1 c.c. = 0·0099 gram (SO_4).
,, 0·1101 N – $Ba(NO_3)_2$, 1 ,, = 0·00485 ,, (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
14·75	0·1460	29·95	0·1453	1·0
14·81	0·1466	30·00	0·1455	0·9
17·35	0·1717	34·90	0·1700	0·6
9·90	0·0980	20·10	0·0975	0·5
			Average error............	0·75

Solutions of coloured sulphates, such as those of copper and nickel, were also tried, the error in these cases ranging from 0·1 to 0·8 per cent. of the theoretical.

From a study of these results it appears that a single titration will come within 1 per cent. of the value found by gravimetric estimation, and, if a sufficient number of titrations are made, the results can be obtained to within 0·5 per cent. of the gravimetric value (compare Table I.). It may be added that the presence of free acid materially aids the precipitation, greatly increasing the rate of precipitation of the turbid liquid in the narrow tube.

The determination of sulphur in iron pyrites by this method gave :

	Gravimetric.	*Volumetric.*
Iron salts present.........	52·13 per cent.	52·20 per cent.
Iron salts absent	52·24 ,,	52·09 ,,

It would seem that this method might be used in cases where speed is of more importance than absolute accuracy. It has this great advantage, that an estimation agreeing within 0·5 per cent. of the best gravimetric method can be made in from three-quarters to one hour ; that is, by taking the mean of four or five volumetric readings.

The Determination of Sucrose by Fehling's Solution.

Experiments with this apparatus were made to determine the best conditions under which the above could be most accurately carried out.

TABLE IV.

	No. of c.c. of sucrose taken.	Equal to gram sucrose.	Dilution in c.c.	Time of heating in minutes.	No. of c.c. of solution used.	Equal to gram sucrose.	Error in per cent.
(1)	10·00	0·2278	200	5	45·50	0·2275	0·2
(2)	10·00	0·2278	150	5	45·65	0·2283	0·3
(3)	5·00	0·1136	100	5	22·75	0·1138	0·2
(4)	10·00	0·2278	150	5	45·64	0·2282	0·2
(5)	10·01	0·2280	150	5	45·58	0·2279	0·1
(6)	10·00	0·2278	175	5	45·62	0·2281	0·1
(7)	10·00	0·2278	150	8	45·65	0·2283	0·3
(8)	2·00	0·0456	200	5	9·02	0·0451	1·0
(9)	5·00	0·1136	450	5	22·90	0·1145	1·0
(10)	10·00	0·2278	450	5	45·92	0·2296	0·9
(11)	10·00	0·2278	150	15	45·82	0·2292	1·0
(12)	5·00	0·1136	100	20	23·20	0·1160	2·0

These results are some of a number of determinations, and they show that, if suitable conditions are obtained, the results give excellent agreement with the theoretical. The conditions are, first, that the Fehling's solution should be added to the boiling liquid to within 1 c.c. of the correct amount, this being obtained by previous rough titrations; secondly, that the strength of the sucrose in the flask should not be more than 0·15 gram in from 75—100 c.c. of water, and thirdly, that the time of heating should not be more than from five to eight minutes.

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CXXVIII.—*A Method for the Determination of the Equilibrium in Aqueous Solutions of Amines, Pseudo-acids and -bases, and Lactones.*

By TOM SIDNEY MOORE.

THE substances mentioned in the title of this paper resemble each other in that their aqueous solutions contain, in addition to ions, two non-ionised forms. Thus a pseudo-acid of which the ketonic form is $H\cdot X{:}O$ gives ions $X\cdot O'$ and $H^{\cdot}$ which correspond with the enolic form $X\cdot O\cdot H$. The relations are expressed by the equations:

$$H\cdot X{:}O \rightleftharpoons X\cdot O\cdot H \rightleftharpoons XO' + H^{\cdot}\,;$$

and similar equations apply to pseudo-bases.

Ammonia, the amines, the lactones, and carbon dioxide differ from pseudo-acids and basos in that the form directly in equilibrium with the ions is formed from the non-ionising part by union with water, so that for an amine the equations are

$$X_3N + H_2O \rightleftharpoons X_3NH{\cdot}OH \rightleftharpoons X_3NH^{\cdot} + OH'.$$

But when the law of mass-action is applied to these equations, the distinction between ammonia, amines, &c., on the one hand, and pseudo-acids and bases, on the other, disappears. For if x be in each case the concentration of the non-ionising part (*e.g.* NH_3, $H{\cdot}X{:}O$), y the concentration of the ionising part (*e.g.* $NH_4{\cdot}OH$, $X{\cdot}OH$), and z the concentration of the ionised part (*e.g.* $NH_4^{\cdot}$, $X{\cdot}O'$):

$$k_1y = z^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{and } y = k_2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_1 and k_2 are constants for each particular substance.* The constants k_1 and k_2 are of considerable theoretical importance, for k_1 is the "true" ionisation constant of the substance and k_2 expresses the relation between the ionising and the non-ionising parts. But so far their values have been determined in only a few particular cases (compare Hantzsch, *Ber.*, 1899, **32**, 576, and subsequent papers; Dimroth, *Annalen*, 1904, **335**, 1; and Chanlaroff, *Annalen*, 1884, **226**, 333), and the properties of the greater number of pseudo-acids and bases and of all the amines are such that the methods used in these cases are not generally applicable.

Hantzsch and Sebaldt (*Zeitsch. physikal. Chem.*, 1899, **30**, 258) and Hantzsch and Vagt (*Zeitsch. physikal. Chem.*, 1901, **38**, 703), from experiments on the variation with temperature of the partition ratios of amines between water and a second solvent, drew conclusions as to the extent of the combination of amine with water in certain cases. These conclusions are, however, of a qualitative nature, and do not give any idea of the relative magnitudes of k_1 and k_2 for different substances.

In the present paper it is shown that the actual values of these two constants can be calculated by combining the results of experiments on the partition of a substance between two solvents, at different temperatures, with the values of the "apparent" ionisation constants (see p. 1377) at the same temperatures.

If two substances, X and Y, are shaken up with two immiscible solvents, such as benzene and water, the relations between the concentrations in the two solutions when equilibrium has been attained are

$$x = P_1x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$y = P_2y' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

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* Equation (1) applies to such substances as form only two ions. The equations developed in this paper would therefore not apply directly to carbon dioxide.

where x and y are the concentrations in the aqueous solution, x' and y' are the concentrations in the benzene solution, and P_1 and P_2 are constants.

If X and Y are the the non-ionising and ionising parts respectively of an amine or pseudo-acid or lactone, we cannot, in general, determine any of the quantities in these equations, but we can determine the total concentration $x' + y'$ in the non-aqueous solution.

Now $x' + y' = \frac{x}{P_1} + \frac{y}{P_2} =$ [from equation (2)] $x \left\{\frac{1}{P_1} + \frac{k_2}{P_2}\right\} = Mx$,

where M is a constant for any particular temperature. Thus the total concentration in the non-aqueous solution is proportional to the concentration of the non-ionising part in the aqueous solution even when both the non-ionising and the ionising parts are soluble in the second solvent.

If now we take two aqueous solutions at the same temperature, giving x, y, and z their previous meanings and putting a for the total concentrations in the aqueous solution, we have

$$x_1 + y_1 = a_1 - z_1 \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$x_2 + y_2 = a_2 - z_2 \quad \ldots\ldots\ldots\ldots \quad (5)$$

and the value of z may be calculated from the electrical conductivity. If these solutions are in equilibrium with two benzene solutions in which the total concentrations are c and c_2 respectively, then

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} \quad \ldots\ldots\ldots\ldots \quad (6).$$

And from equation (2): $\frac{x_1}{x_2} = \frac{y_1}{y_2} \quad \ldots\ldots\ldots \quad (6a).$

We have then four equations containing four unknown quantities, x_1, x_2, y_1, y_2; yet the unknown quantities cannot be found, for on substituting from equations (6) and (6a) in equations (4) and (5), the latter become of the same form. The difficulty disappears only if the conditions are so altered that equation (6a) is no longer true. This shows that the essential condition for the solution of the problem is that the solutions under consideration shall be at different temperatures.

A difference in temperature between the two solutions causes difficulty in that the partition coefficient may, and k_1 certainly does, alter with temperature. It becomes necessary to consider three solutions at temperatures t_1, t_2, t_3, such that $t_2 - t_1 = t_3 - t_2$. For then, if k_1', k_1'', k_1''' are the values of k_1 corresponding to t_1, t_2, t_3 respectively and q is the heat absorbed on ionisation, we have

$\log_e \frac{k_1''}{k_1'} = \frac{q}{R} \frac{t_2 - t_1}{(273 + t_1)(273 + t_2)} = \frac{q}{R} \frac{t_2 - t_1}{(273 + t_2)^2}$ when t_1 and t are near together.

Similarly, $\log_e \dfrac{k_1'''}{k_1''} = \dfrac{q}{R} \dfrac{t_3 - t_2}{(273 + t_2)^2}$.

$$\therefore \frac{k_1''}{k_1'} = \frac{k_1'''}{k_1''} = l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if q is constant over the range of temperature t_1 to t_3.

For the variation of k_2 with temperature we have in the same way:

$$\frac{k_2''}{k_2'} = \frac{k_2'''}{k_2''} = \frac{1}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

If the ionising part of the substance is insoluble in the second solvent, we have similarly for the partition coefficient:

$$\frac{M''}{M'} = \frac{M'''}{M''} = n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

If the solubility of the ionising part in the second solvent is considerable, equation (9) will be no longer strictly true, since M then involves three constants, P_1, P_2, and k_2. But, as may be seen from the calculations in the paper following this, small variations in n may at present be neglected.

Then if x_1, y_1, z_1, a_1, and c_1, are concentrations corresponding to t_1
,, x_2, y_2, z_2, a_2 ,, c_2 ,, ,, t_2
,, x_3, y_3, z_3, a_3 ,, c_3 ,, ,, t_3

where x = conc. of non-ionising part in aqueous sol. (*e.g.* NH_3)
,, y = ,, ionising ,, (*e.g.* $NH_4 \cdot OH$)
,, z = ,, ionised ,, (*e.g.* $NH_4^{\cdot}$)
,, a = total concentration in aqueous solution = $x + y + z$
,, c = ,, non-aqueous solution;

and, further, putting

$$\frac{c_1}{c_2} = r_1, \ \frac{c_2}{c_3} = r_2, \ \frac{t_1^2}{t_2^2} = s_1, \ \frac{t_2^2}{t_3^2} = s_2;$$

we have:

$$x_1 + y_1 = a_1 - z_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10).$$

$$x_2 + y_2 = a_2 - z_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11).$$

$$x_3 + y_3 = a_3 - z_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

And

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} \cdot \frac{M''}{M'} = r_1 n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13).$$

$$\frac{x_2}{x_3} = \frac{c_2}{c_3} \cdot \frac{M'''}{M''} = r_2 n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

From equation (1):

$$\therefore \quad \frac{y_1}{y_2} = \frac{t_1^2}{t_2^2} \cdot \frac{k_1''}{k_1'} = s_1 l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

and, similarly, $\dfrac{y_2}{y_3} = s_2 l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$

Of these quantities, the values a and c are determined experimentally, and the values of z are determined from the "apparent" ionisation constants. So that r_1, r_2, s_1, s_2 are known.

From equations (10), (11), (13), (15):

$$y_2(s_1l - r_1n) = a_1 - z_1 - r_1n(a_2 - z_2) \quad . \quad . \quad . \quad (17).$$

Similarly,

$$y_3(s_2l - r_2n) = a_2 - z_2 - r_2n(a_3 - z_3) \quad . \quad . \quad . \quad (18).$$

Hence,

$$s_2l\,\frac{s_1l - r_1n}{s_2l - r_2n} = \frac{a_1 - z_1 - r_1n(a_2 - z_2)}{a_2 - z_2 = r_2n(a_3 - z_3)} \quad . \quad . \quad . \quad (19).$$

Further, by applying equation (2) to the solutions at t_1 and t_2, we get

$$\frac{y_1}{y_2} = \frac{k_2'}{k_2''}\cdot\frac{x_1}{x_2}$$

$$\therefore \quad \frac{s_1}{r_1} = \frac{mn}{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20a).$$

Similarly,

$$\frac{s_2}{r_2} = \frac{mn}{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20b).$$

Again, if the observed values of the electrical conductivity for a substance which exists in two non-ionised forms are substituted in the equation for the ionisation constant of an ordinary binary electrolyte,

$$K = \frac{\lambda_v^2}{v\lambda_a(\lambda_a - \lambda_v)},$$

K is found to be a constant and is generally called the ionisation constant, although, as we have seen, the "true" ionisation constant for such a substance is the quantity we have called k_1. Kauffman (*Zeitsch. physikal. Chem.*, 1904, **47**, 618), has shown that the constant K, which we shall call the "apparent" ionisation constant, is connected with the constants k_1 and k_2 by the relation

$$K(1 + k_2) = k_1k_2.$$

Applying this equation to solutions at t_1 and t_2, we get

$$\frac{K'}{K''}\cdot\frac{1 + k_2'}{1 + k''} = \frac{k_1'}{k_1''}\cdot\frac{k_2'}{k_2''} = \frac{m}{l} \quad . \quad . \quad . \quad . \quad (21a).$$

Similarly,

$$\frac{K''}{K'''}\cdot\frac{1 + k_2''}{1 + k_2'''} = \frac{m}{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21b).$$

Eliminating k_2', k_2'' and k_2''' between equations (8), (21a), and (21b), we get a quadratic in m of which the two roots are

$$m = 1 \text{ and } m = \frac{lA_1(lA_2 - 1)}{lA_1 - 1} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $\frac{K'}{K''} = A_1$ and $\frac{K''}{K'''} = A_2$.

The root $m = 1$ is impossible, since on substitution in the above equations it gives a negative value for k_2. The root required therefore is given by equation (22).

We now have nine equations (10 to 16 and 20 and 22) containing nine unknown quantities (x_1, x_2, x_3, y_1, y_2, y_3, l, m, and n), all of which may therefore be determined. The most convenient method is to take the three equations, (19), (20), and (22), from which values of l, m, and n may be obtained; y_1, y_2, y_3, &c., may then be calculated from equations (17) and (18).

From equations (20a) and (20b) we see that if the temperature coefficients remain constant over the range of temperature $t_1 - t_3$, then

$$\frac{s_1}{r_1} = \frac{s_2}{r_2},$$

so that if the assumption that q is constant (p. 1376) is justified, this relation will be fulfilled, and, although the converse statement is not necessarily true, it is extremely probable. So that if in any particular case the values of $\frac{s}{r}$ are found to be constant, we may conclude that l, m, and n are constant over the range of experiment.

Since the values of the temperature coefficients l, m, and n are given by the equations, the heat changes corresponding with the transition of the ketonic to the enolic form of a pseudo-acid or base, or to the hydration of an amine and to the ionisation, may be calculated. From these quantities the heat of neutralisation may be found, and the comparison of the result so obtained with the result of experiment gives a means of checking the accuracy of the method.

No account has been taken of the variation of the partition coefficient with concentration, although such a variation has been found by Hantzsch and Vagt (*loc. cit.*) and by Dawson and McCrae (Trans., 1901, **79**, 496, 1072, and 1906, **89**, 1666). But when the laws governing this variation are known, it should not be difficult to introduce a correction into the above equations. And it should further be stated that the method of calculation does not deal with the question of the existence of non-ionising hydrates (which may be written, for example, NH_3,H_2O) as distinct from ionising hydroxides (for example, $NH_4 \cdot OH$). Such compounds may, of course, be present in aqueous solutions, and would with the non-hydrated compound (for example, NH_3) form what has been called in this paper the non-ionising part.

Examples of the application of these equations are given in the following paper, and the author is proceeding with the further experimental investigation of the subject.

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CXXIX.—*The "True" Ionisation Constants and the Hydration Constants of Piperidine, Ammonia, and Triethylamine.*

By **Tom Sidney Moore.**

In three cases the data necessary for the application of the equations developed in the preceding paper have been published already, and it seemed to the author advisable to publish the results of the calculations in these cases without waiting for the results of further experimental investigation.

(1) *Piperidine.*—The partition coefficients of piperidine between water and benzene at temperatures from 5·5° to 50°, and values of the apparent ionisation constant over the same range of temperature, are given by Hantzsch and Sebaldt (*Zeitsch. physikal. Chem.*, 1899, **30**, 259). Their results were plotted out, and the numbers used in the calculations (given in the first four columns of the following table) were read off from the smooth curves most nearly representing the results.

Temperature.	Percentage of piperidine in benzene layer.	Percentage of piperidine in aqueous layer.	$K \times 100$.	s/r.
5°	27·93	72·07	0·0973	
				1·121
10	31·44	68·56	0·1040	
				1·121
15	34·95	65·05	0·1100	
				1·122
20	38·43	61·57	0·1153	
				1·125
25	41·92	58·08	0·1200	
				1·129
30	45·42	54·58	0·1240	
				1·152
35	48·90	51·10	0·1250	

From these numbers the values of r, s, and A are calculated, and the values of $\frac{s}{r}$* are tabulated in the last column of the table; the constancy of the value of this ratio shows that we are justified in the assumption that l, m, and n are constant over the range of experiment (see p. 1378).

The further calculation was carried out as follows. From equation (20) (p. 1377), by putting $n = 1$ (for in all cases where the partition of a substance which has no peculiarity of ionisation has been investigated, it has been found that the partition coefficient varies only slightly with the temperature, that is, n is nearly unity), we get a value for $\frac{m}{l}$; substituting this in equation (22) we get a simple equation in l, the value of which may then be calculated. Now there are two ways of testing the truth of the assumption that $n = 1$. The first by substituting $n = 1$ and the value of l found as above in equation (19); if this equation is satisfied within the limits due to experimental error, the values of l and n used satisfy the three equations (19), (20), and (22), that is, are the values required. The second method is to put $n=1$ in equation (19) and to solve the quadratic in l which results. Of the two roots obtained, the smaller always gave negative values for one of the concentrations, so that the larger root is the one required.

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* The symbols have the same meaning as in the preceding paper.

Range of temperature $=t_1-t_3$.	l from equation (22).	l from equation (19).	Result of substituting $n=1$ and values of l from equation (22) in equation (19).
5—15	1·129	1·126	−0·0008
10—20	1·111	1·108	−0·0003
15—25	1·092	1·090	±0·0
20—30	1·086	1·070	+0·012
25—35	(1·202)	(1·13)	(+0·079)
Mean.........	1·105		

The value of each side of equation (19) is about 1·2, so that the errors shown in the last column are surprisingly small. The assumption that $n=1$ is justified in this case.

From these values of l and n the values of x and y may be calculated by equation (17) and (18), and y for any particular temperature may be calculated from two distinct equations. Thus y_{15} may be calculated from experiments at 10° and 15°, or from experiments at 15° and 20°. The mean of the two values thus obtained has been taken as the true value of y in each case, and has been used in the calculation of the other quantities given in the following table:

Temperature to which values correspond.	Temperatures corresponding to equations from which y is found.	y.	y (mean).	x.	$k_2=y/x$.	$k_1\times100$.	$\frac{\text{Conc. of } C_5H_{10}NH \text{ in aqueous sol.}}{\text{Conc. of } C_5H_{10}NH \text{ in benzene sol.}}$
5°	5—10°	0·0157	0·0157	0·00258	6·09	0·1133	0·30
10	5—10 10—15	0·0143 0·0140	0·0141	0·00307	4·60	0·1266	0·31
15	10—15 15—20	0·0125 0·0125	0·0125	0·00361	3·47	0·1417	0·33
20	15—20 20—25	0·0111 0·0112	0·0111	0·00393	2·83	0·1560	0·33
25	20—25 25—30	0·0098 0 0101	0·0100	0·00406	2·46	0·1687	0·31
30	25—30	0·0088	0·0088	0·00424	2·08	0·1837	0·30

Accuracy of Results for Piperidine.—To find the effect of an error in the value of n, the equations for the range 15—20° were solved on the assumption that $n=1·02$, with the following results:

l from equation (22).	l from equation (19).	Result of substituting $\left\{\begin{array}{l} l=1·099. \\ \alpha=1·02. \end{array}\right.$ in equation (19).
1·099	1·106	−0·001

$y_{20}=0·01105.$ y_{25} 0·00976.

Thus an error of 2 per cent. on n cannot be detected by this method; but this is of little importance, since the error produced by such a change in l is little more than 1 per cent., and the error on y is less than 1 per cent.

The maximum difference in the two values of y given in the above table is 3 per cent. At 15° such an error would produce an error of 8 per cent. on x, 11 per cent. on k_2, 2·5 per cent. on k_1, and 8 per cent. on the partition coefficient given in the last column.

Heat of Neutralisation of Piperidine.—Taking l as 1·09 and $\frac{m}{l}$ as 1·125, and using the ordinary formula

$$\log_e\frac{k''}{k'} = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

we find the heat changes involved in the hydration and ionisation of piperidine are:

$$C_5H_{10}NH + H_2O = C_5H_{10}NH_2OH + 7000 \text{ cals.}$$
$$C_5H_{10}NH_2{\cdot}OH = C_5H_{10}NH_2^{\cdot} + OH' - 2960 \text{ cals.}$$

The heat of neutralisation of a solution of piperidine is thus equal to $13{\cdot}7 + 7x - 2{\cdot}96(x+y)$ larger calories, where x and y are the amounts of $C_5H_{10}NH$ and $C_5H_{10}NH_2OH$ respectively in the volume of solution containing 1 gram-molecule. (The heat changes due to incomplete ionisation of the acid and of the salt formed have been neglected.)

For a semi-normal solution this equation gives the value 12·7 larger calories. Colson (*Ann. Chim. Phys.*, 1890, [vi], **19**, 408) found 13·02 at 15°; Berthelot (*Thermochimie*, II, 646) found 13·32 at 22°.

(2) *Ammonia.*—Both Hantzsch and Sebaldt (*loc. cit.*) and Dawson and McCrae (Trans., 1900, **77**, 1239; 1901, **79**, 1072; 1906, **89**, 1666) have determined the partition coefficient of ammonia between water and chloroform at different temperatures. The results of the latter authors are the more accurate, and have been used in the calculations; but since experiments were carried out at three temperatures only, 10°, 20°, 30°, interpolation for 15° and 25° was impossible. These three temperatures were therefore taken as t_1, t_2, and t_3.

Hantzsch and Sebaldt give also values of the apparent ionisation constant of ammonia at different temperatures, but, as is immediately apparent on plotting out the numbers, they are not sufficiently accurate to serve as a basis for calculation. The values of K used were obtained by combining the results of Kohlrausch (*Sitzungsber. k. Akad. Berlin,* 1900, 1002, and 1901, 1031) with the conductivity measurements of Kohlrausch, Bredig, and Hantzsch.

Temperature.	$K \times 100$.	Concentration in chloroform layer.	a.	s/r.
10°	0·00169	0·01352	0·3917	1·045
20	0·00190	0·01588	0·3917	1·088
30	0·00203	0·01846	0·3917	

The condition that $\frac{s}{r}$ should be constant is not so well fulfilled in this case as with piperidine. But, since ammonia is one of the most interesting cases, the calculation was carried out with the mean value of $\frac{s}{r}$; the constants obtained must show at least the proper order of magnitude, and the striking agreement between the calculated and found heat effects (see below and p. 1383) indicates that the results are very near the truth.

$$\left.\begin{array}{l}\text{Putting } n=1,\ l \text{ from equation } (22)=1{\cdot}52\\ \phantom{\text{Putting } n=1,\ } l \quad ,, \qquad\quad ,, \qquad (19)=1{\cdot}32\end{array}\right\}\text{Mean, } 1{\cdot}42.$$

Using the mean value of l, we get the following table:

Temperature.	y.	x.	$y/x = k_2$.	$k_1 \times 100$.	$\frac{\text{Conc. of NH}_3\text{ in water.}}{\text{Conc. of NH}_3\text{ in chloroform.}}$
10°	0·178	0·213	0·836	0·00368	15·8
20	0·141	0·251	0·560	0·00523	15·5
30	0·106	0·285	0·372	0·00743	15·4

Using the two values of l, 1·52 and 1·32, we find that at 20°

$$\begin{array}{llll} k_1 \text{ is between} & 6{\cdot}5 \times 10^{-5} & \text{and} & 4{\cdot}0 \times 10^{-5}, \\ k_2 \quad ,, & 0{\cdot}42 & ,, & 0{\cdot}70. \end{array}$$

Heat of Neutralisation of Ammonia.—Taking l as 1·42 and m as 1·52, we find:

$$NH_3 + H_2O = NH_4{\cdot}OH + 7190 \text{ cals.}$$
$$NH_4{\cdot}OH = NH_4{}' = OH' - 6030 \text{ cals.}$$

from which the heat of neutralisation of a 0·278 N-solution of ammonia at 20° is found to be 12·3 larger calories. Thomsen (*Thermochemische Untersuchungen*) found 12·25 for a solution of this strength at 17·5°.

Heat of Solution of Ammonia.—Perman (Trans., 1903, **83**, 1174) has determined the partial pressure of ammonia in the vapour of its solution at various temperatures and concentrations. The ratio between the partial pressure and the concentration of NH_3 (as distinct from $NH_4{\cdot}OH$ and its ions) in the solutions is the partition coefficient of ammonia between the two phases, and Perman's results might therefore be used to calculate the values of k_1 and k_2 by the above method. But n is not equal to unity in this case, since the act of solution is accompanied by considerable heat changes, and it is thus easier to show that the results already obtained for ammonia are in agreement with Perman's results by calculation of the heat of solution, than by the direct application of the equations to the values of the vapour pressure.

Temperature.	a.	Partial pressure of NH_3 in mm. of Hg.	x = concentration of NH_3.	$\frac{x}{\text{partial pressure}} = P$.	$\frac{Pt_1}{Pt_2} = n$.
10°	1·456	9·0	0·790	0·0879	1·46
20	1·453	15·5	0·930	0·0600	1·42
30	1·450	25·0	1·057	0·0430	
				Mean ...	1·44

The first three columns are from Perman's tables; x is calculated from a by means of the values of k_1 and k_2 (preceding page); P is the partition coefficient of NH_3 between the two phases, and the last column gives the variation of P with temperature.

Applying van't Hoff's formula to this temperature coefficient, we find that the act of solution (apart from any hydration or ionisation) of one gram-molecule of ammonia in water is accompanied by an evolution of 6270 calories. Then the heat actually observed on solution of one gram-molecule is

$$6{\cdot}27 + 7{\cdot}19\,(y + z) - 6{\cdot}03\,z \text{ large calories,}$$

where y and z are the quantities of $NH_4{\cdot}OH$ and $NH_4^{\cdot}$ respectively in the resulting solution, and may be calculated from the values of k_1 and k_2 given above. For a solution approximately $0{\cdot}3N$ at 20° this quantity is found to be 8·83 larger calories. Thomsen (*Thermochemische Untersuchungen*, II., 73) finds 8·44 for the same strength of solution and temperature; Berthelot (*Thermochimie*, II., 69) finds 8·82 at 10°.

(3) *Triethylamine.*—The partition coefficients are from the results of Hantzsch and Vagt (*Zeitsch. physikal. Chem.*, 1901, 38, 703). Hantzsch and Sebaldt give values for the apparent ionisation constant at different temperatures, but no curve can be drawn which represents them all. By neglecting the numbers for 10° and 40°, a fairly good curve was obtained from which the values used in the calculation were read off.

Temperature.	c.	a.	100 K.	s/r.
15°	0·0503	0·01224	0·0387	1·092
20	0·0516	0·01091	0·0414	1·088
25	0·0526	0·00987	0·0435	1·088
30	0·0535	0·00897	0·0453	1·079
35	0·0542	0·00828	0·0468	

The calculations were carried out exactly as in the case of piperidine, and n was found equal to unity within the limits of experimental error:

$$\text{Mean value of } l = 1{\cdot}19.$$

$$\text{,,} \quad \text{,,} \quad \frac{m}{l} - 1{\cdot}09.$$

Temperature.	Temperature of observations used.	y.	y (mean).	x.	$y/x = k_2$.	$k_1 \times 100$.	$\frac{x}{\text{Conc. in toluene}}$
15°	15—20°	0·00732	0·00732	0·00293	2·50	0·054	0·058
20	15—20	0·00597	0·00584	0·00314	1·86	0·064	0·061
	20—25	0·00571					
25	20—25	0·00466	0·00467	0·00333	1·40	0·075	0·063
	25—30	0·00467					
30	25—30	0·00381	0·00385	0·00334	1·15	0·085	0·062
	30—35	0·00389					
35	30—35	0·00318	0·00318	0·00335	0·95	0·096	0·062

At 20°: $N(C_2H_5)_3 + H_2O = N(C_2H_5)_3H{\cdot}OH + 9000$ cals.
$N(C_2H_5)_3H{\cdot}OH = N(C_2H_5)_3H^{\cdot} + OH' - 6060$ cals.

Heat of neutralisation of a semi-normal solution = 10·9 larger cals.
Berthelot (*Thermochimie*, I., 699) found = 9·6 „ „

The results communicated in this paper are neither sufficiently numerous nor based on sufficiently accurate data to warrant much discussion. One point is worthy of remark: for ammonia and triethylamine at 20° the values of k_1 are $5{\cdot}23 \times 10^{-5}$ and $6{\cdot}4 \times 10^{-4}$, so that the introduction of three ethyl groups into ammonia has increased the constant only twelve-fold. Now the introduction of a fourth ethyl group gives tetraethylammonium hydroxide, the degree of ionisation of which is comparable with that of sodium hydroxide. It is difficult to imagine that this large change of ionisation is produced solely by the introduction of the fourth ethyl group when the first three have produced a comparatively small effect. These results point rather to a difference in constitution between the quaternary ammonium hydroxides and the hydroxides of primary, secondary, and tertiary amines (compare Werner, *Ber.*, 1903, **36**, 147; Hantzsch, *Ber.*, 1905, **38**, 2161).

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CXXX.—*The Application of Baeyer's Reduction to Benzoin and its Derivatives.*

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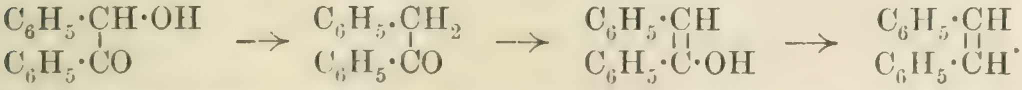
IT has been shown in a previous paper (Trans., 1907, **91**, 536) that both *o*- and *p*-dimethoxybenzoins behave abnormally when reduced by Baeyer's process, giving unsaturated hydrocarbons which have no simple relationship to the parent benzoins. In the case of anisoin it was proved that the reduction proceeded through the intermediate formation of deoxyanisoin and *p*-dimethoxystilbene, with the ultimate production of stilbene. In view of this result, we have applied Baeyer's method of reduction to ordinary benzoin and also to a number of its derivatives, and have found that the reaction follows the same irregular course, deoxybenzoin being first produced and this in turn being directly converted into stilbene. It has already been noted (*Annalen*, 1870, **155**, 90; 1888, **248**, 7) that small quantities of stilbene are produced when benzoin is reduced, either by heating with zinc dust alone or in presence of acetic acid, but the mechanism of the reduction has not hitherto been investigated.

As in previous cases (*loc. cit.*), we find that evidence bearing on the course of the reaction is obtained by carrying out the distillation with zinc dust at the lowest possible temperature in a rapid stream of carbon dioxide. Under these conditions, deoxybenzoin was the sole product, and no hydrocarbons were detected in the distillate. When, on the other hand, a current of hydrogen was used, the reduction product consisted almost entirely of stilbene together with small quantities of dibenzyl and di- and tetra-hydrophenanthrenes. The amount of dibenzyl obtained was, however, extremely small, in spite of the fact that it is the hydrocarbon most closely related to benzoin. It is, of course, known (*Annalen*, 1870, **154**, 177) that dibenzyl is converted at a dull red heat into stilbene, and it appeared possible that the former might have been the normal reduction product, but had subsequently been decomposed into the unsaturated hydrocarbon. Experiments on the reduction of deoxybenzoin, however, showed that this was not the case, as, when distilled with zinc dust at the lowest possible temperature in an atmosphere of carbon dioxide, no dibenzyl was produced and stilbene was the only product. This result is in agreement with the explanation of similar reductions, which was suggested in a previous paper, that the ultimate formation of an unsaturated hydrocarbon is due to the reduction of the enolic form of deoxybenzoin.

According to this view, the series of changes involved is shown below:



$$\begin{array}{l}C_6H_5\cdot CH\cdot OH\\ \quad\;\; |\\ C_6H_5\cdot CO\end{array} \longrightarrow \begin{array}{l}C_6H_5\cdot CH_2\\ \quad\;\; |\\ C_6H_5\cdot CO\end{array} \longrightarrow \begin{array}{l}C_6H_5\cdot CH\\ \quad\;\; \|\\ C_6H_5\cdot C\cdot OH\end{array} \longrightarrow \begin{array}{l}C_6H_5\cdot CH\\ \quad\;\; \|\\ C_6H_5\cdot CH.\end{array}$$

The small quantities of the hydrides of phenanthrene which were obtained are doubtless decomposition products of the stilbene itself.

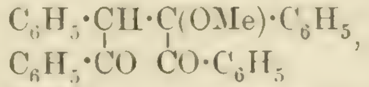
The alternative explanation that deoxybenzoin loses a molecule of water to give tolane, which afterwards undergoes partial saturation to stilbene, was negatived by experiments in which deoxybenzoin was distilled repeatedly in a current of carbon dioxide through a hot combustion tube filled with pumice, no tolane or other hydrocarbon being detected in the product.

The reduction of a number of benzoin derivatives with varying side-chains showed the same generalisations as were found to exist in the case of anisoin, the group $\begin{array}{l}\cdot CH\cdot OR \\ | \\ \cdot CO\end{array}$ reducing in the first place to $\begin{array}{l}\cdot CH_2 \\ | \\ \cdot CO\end{array}$, whilst $\begin{array}{l}\cdot CH\cdot OR \\ | \\ \cdot CH\cdot OR_1\end{array}$ was converted directly into $\begin{array}{l}\cdot CH \\ \| \\ \cdot CH\end{array}$. The results are summarised in the following table:

Substance.	Conditions of experiment.	Products.
1. Benzoin	Distilled in carbon dioxide	Deoxybenzoin
2. Benzoin methyl ether	,, ,, ,,	Deoxybenzoin; stilbene
3. Deoxybenzoin	,, ,, ,,	,, ,,
4. Hydrobenzoin	,, ,, ,,	Stilbene
5. Hydrobenzoin methyl ether.	,, ,, ,,	,,
6. Hydrobenzoin dimethyl ether	,, ,, ,,	,,
7. Benzil	,, ,, ,,	Benzil
8. Benzoin	Distilled in hydrogen	Stilbene
9. Deoxybenzoin	,, ,,	,,
10. Benzoin methyl ether	,, ,,	,,
11. Benzil	,, ,,	,,

Invariably the reductions proceeded much more easily than was the case with substituted benzoins; in particular the ketonic group in deoxybenzoin or benzil showed the readiest tendency to undergo reduction. The partial reduction of benzoin to deoxybenzoin or its complete reduction to stilbene are, in fact, reactions which are so readily controlled that the process can be recommended as a practical method of rapidly preparing these compounds.

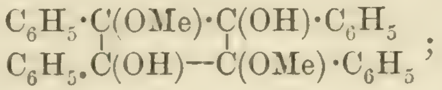
We have extended our work by examining the behaviour of deoxybenzoin towards various reagents, with the hope of detecting indications of the compound reacting in the enolic form. These experiments, which on the whole gave negative results, are summarised in the experimental part. Reference is also made to the formation of two hitherto unknown compounds which were isolated during the preparation of benzoin methyl ether. The latter was prepared in the first instance by Fischer's method (*Ber.*, 1893, **26**, 2412), in which a methyl-alcoholic solution of benzoin is saturated with hydrogen chloride. Fischer states that, at first, the solution must be maintained at 40—50°, in order "to prevent the separation of the dissolved benzoin." In spite of this precautions, a quantity of crystalline matter separated, which, as it did not resemble benzoin in crystalline form, was removed and examined. Two compounds were isolated from this product by fractional crystallisation, one of which melted at 185°, the other at 285°. The former proved to be a condensation compound produced by the elimination of a molecule of water from a molecule of benzoin and one of benzoin methyl ether. It therefore has the composition



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot \underset{|}{C}(OMe)\cdot C_6H_5 \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array},$$

and, when hydrolysed with 20 per cent. hydrochloric acid, was resolved into benzoin and benzoin methyl ether.

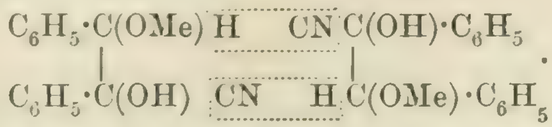
Greater interest attaches itself to the compound of higher melting point which gave the same analytical figures as benzoin methyl ether, but possessed a molecular weight twice as great. The substance, which was sparingly soluble in all reagents, did not affect Fehling's solution, and resisted the action of even boiling concentrated hydrochloric acid. The most probable formula which can be ascribed to the compound is



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}(OMe)\cdot \underset{|}{C}(OH)\cdot C_6H_5 \\ C_6H_5.C(OH)-C(OMe)\cdot C_6H_5 \end{array};$$

this represents it as a product of the union of 2 molecules of benzoin methyl ether in a manner resembling the benzoin condensation.

The above compounds are not to be regarded as intermediate substances in the formation of benzoin methyl ether, as they were recovered unchanged after being shaken for several days at 40° with excess of alcoholic hydrogen chloride. The formation of the tetramethylene derivative seems in some way to be dependent on the presence of traces of nitrogen compounds, occurring as impurities in the benzoin used, and it is possible that its production is due to the temporary addition and subsequent elimination of hydrogen cyanide from the benzoin ether. Clarke and Lapworth (Trans., 1907, **91**, 694) have recently drawn attention to the fact that the hydrogen atom in a ·CH group, which is attached to the benzene ring and also to the nitrile group, is capable of lability. Assuming that, during the methylation, hydrogen cyanide is produced and forms the cyanohydrin of benzoin methyl ether, the hydrogen atom of the ·CH·OMe group may be eliminated together with the nitrile group of another molecule, thereby effecting the condensation



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}(OMe)\ \boxed{H\quad CN}\ \underset{|}{C}(OH)\cdot C_6H_5 \\ C_6H_5\cdot C(OH)\ \boxed{CN\quad H}\ C(OMe)\cdot C_6H_5 \end{array}.$$

Further experiments, in which benzoin methyl ether was subjected under various conditions to the action of hydrogen cyanide, seemed, however, to indicate that the latter was not the active agent in bringing about the condensation, which possibly may depend on the presence of nitriles produced from benzaldehyde and therefore only present in crude benzoin.

The subject is at present engaging our attention, and we mean to carry out similar experiments on the ethers of substituted benzoins.

EXPERIMENTAL.

Reduction of Benzoin to Deoxybenzoin.

The benzoin was mixed in quantities of not more than 10 grams with a large excess of zinc dust, and distilled over pumice stone with which zinc dust was incorporated. The distillation was carried out rapidly at the lowest possible temperature, and during the experiment a brisk current of dry carbon dioxide was led through the apparatus. Copious white fumes were evolved, which together with the oily product were absorbed by passing into alcohol. The experiment was easily controlled so that no stilbene was produced, and on recrystallising the product from light petroleum, deoxybenzoin was obtained which melted at 59—60°, and was identified by conversion into the oxime melting at 98°. The average yield was more than 60 per cent. of the theoretical amount, and, in all, 30 grams of benzoin were in this way converted into 17 grams of pure deoxybenzoin.

On account of the ease with which the product is obtained in a pure condition, the method is a convenient one for preparing small quantities of deoxybenzoin. When obtained from benzoin by the action of zinc dust and acetic acid (Trans., 1897, **71**, 219) or alcoholic hydrogen chloride (*Ber.*, 1888, **21**, 1296), the compound is somewhat difficult to purify by crystallisation, and is contaminated with hydrobenzoin and tetraphenylethane.

Conversion of Benzoin into Stilbene.

This reduction was carried out exactly as in the previous case, except that the distillation was conducted more slowly and a dull red heat was employed. Even in an atmosphere of carbon dioxide good yields of stilbene were obtained, but when a current of hydrogen was used, the product was quite free from deoxybenzoin and the yield was materially increased. The semi-solid distillate was collected in alcohol and recrystallised from the same medium. The product melted at 124°, and was further identified as stilbene by its conversion into the α-dibromide (m. p. 237°). When only 5 grams of benzoin were used in each experiment, the yield of stilbene was 70 per cent. of the calculated amount, but in experiments on a larger scale this was reduced to 55 per cent. In this way, 70 grams of the pure hydrocarbon were obtained from 150 grams of benzoin. This yield compares very favourably with that obtained by other processes; when prepared respectively from dibenzyl, phenyl cinnamate, or from dichloro-ether, the hydrocarbon is only produced in amounts corresponding to 54, 12, and 25 per cent. of the calculated weights, whilst the operations require a much longer time. In larger preparations, we distilled the benzoin from a retort in a current of hydrogen through a wide tube packed with pumice and zinc dust. The yield of stilbene obtained in this way was, however, not so great as when the ordinary method was used.

During the recrystallisation of the crude stilbene, a small quantity of a pale yellow oil was recovered from the mother liquors. This oil has already been isolated as a product of benzoin reductions, and Limpricht and Jena (*loc. cit.*), who proved it to have the composition $C_{14}H_{12}$, regarded it as a polymeride of stilbene. The oil was distilled in steam and afterwards fractionated at the ordinary pressure. The various distillates deposited a quantity of crystals which proved to be stilbene containing a little dibenzyl. Repeated fractionation of the oil gave two liquids, one boiling at 270—275°, the other at 305—310°. As both liquids solidified to a crystalline mass when cooled to $-5°$, and, when distilled with zinc dust, yielded a mixture of stilbene and phenanthrene, we regard them as di- and tetra-hydrophenanthrenes.

Effect of Substituting other Metals for Zinc in the Reduction of Benzoin.

The use of zinc dust as the reducing agent is not altogether free from objection. Different specimens show great variation in their efficacy, and in carrying out Baeyer's reduction on a large scale we have detected the presence of hydrogen arsenide in the gases evolved from the distillation tube, and in some cases the crude stilbene was contaminated with free arsenic. In order to avoid this, we have tried the effect of substituting other metals for zinc dust. When levigated iron was used, the reduction proceeded with some difficulty, and, although stilbene was the main product, a quantity of deoxybenzoin was formed, even when the distillation was carried out in a current of hydrogen. The yield of the hydrocarbon was considerably smaller than when zinc dust was used. Similar results were obtained by the use of well-reduced iron filings.

Duplicate experiments with magnesium powder showed that the latter reacts much too energetically, as, in addition to stilbene, a considerable amount of benzaldehyde was obtained and a quantity of carbonaceous matter remained undistilled. Aluminium powder behaved in a similar fashion, and in no case were such satisfactory results obtained as when zinc dust was used.

Preparation and Reduction of Benzoin Derivatives.

Hydrobenzoin.—The hydrobenzoin was prepared by the same method as that previously adopted for the preparation of hydroanisoin (*loc. cit.*), a solution of benzoin in wet ether being treated with sodium amalgam, while the liquid was kept neutral by a stream of carbon dioxide. The yield of pure product was 85 per cent. of the theoretical amount, and it should be noted that no deoxybenzoin and only a trace of *iso*hydrobenzoin was produced.

When distilled with zinc dust, either in carbon dioxide or hydrogen, stilbene was formed.

Hydrobenzoin Monomethyl Ether.—This compound was prepared by reducing benzoin methyl ether by the method referred to above. The product when recrystallised from a mixture of alcohol and light petroleum consisted of small prisms melting at 100—102°. Analysis gave:

C = 78·94 ; H = 7·02 ; MeO = 14·34.

$C_{15}H_{16}O_2$ requires C = 78·83 ; H = 7·16 ; MeO = 13·60 per cent.

The reduction with zinc dust gave the same results as in the case of hydrobenzoin.

Hydrobenzoin dimethyl ether was prepared by the silver oxide method of alkylation. Hydrobenzoin (1 mol.) was dissolved in methyl iodide (4 mols.) containing a little acetone, and dry silver oxide (2 mols.) gradually added. The reaction was very vigorous. After heating for ten hours on a water-bath, the mixture was worked up as usual. The crystalline product contained, however, some unaltered hydrobenzoin, and accordingly the alkylation was repeated, no acetone being required in this case. The desired compound was thus obtained in large prisms which, when recrystallised from ether, melted at 140—142°. Analysis gave:

C = 78·98 ; H = 7·62 ; MeO = 24·82.

$C_{16}H_{18}O_2$ requires C = 79·34 ; H = 7·44 ; MeO = 25·62 per cent.

It will be seen that the compound possesses a higher melting point than either hydrobenzoin or the monomethyl ether, the introduction of one methyl group into the hydroxylic position in hydrobenzoin lowering the melting point, whilst complete methylation raises it considerably. A parallel exists in the case of methyl tartrate, which has a lower melting point than dimethyl dimethoxysuccinate (Trans., 1901, **79**, 957). The molecular weight was determined in benzene solution by the cryoscopic method and found to be normal (found, 236; calculated, 242).

The reduction with zinc dust, which had to be conducted slowly on account of the volatility of the compound, gave stilbene as the sole product.

Benzoin Methyl Ether.—As explained in the introduction, Fischer's method was adopted for preparing this compound, and we also made use of the silver oxide process. Lander (Trans., 1900, **77**, 734) states that in the preparation of benzoin ethyl ether by the latter method a considerable quantity of benzaldehyde is produced, but this may have been due to the fact that the benzoin was not completely dissolved by the alkyl halide. Accordingly sufficient acetone was in this case added to the methyl iodide to effect complete solution of the benzoin, and after one alkylation an oil was obtained which crystallised completely; after recrystallisation from light petroleum, the compound melted at 51—52°. The yield was almost quantitative and the substance crystallised with much greater ease than when prepared by the hydrochloric acid method.

Examination of the By-products obtained in Fischer's Methylation of Benzoin.

On passing dry hydrogen chloride into a solution of 20 grams of benzoin in 300 grams of methyl alcohol at 40—50°, a crystalline precipitate weighing 5 grams separated when the liquid was nearly saturated with the gas. This was collected, washed with alcohol, and recrystallised from benzene. A crop of irregular plates melting at 285° was thus obtained, whilst from the mother liquor a second compound, melting after recrystallisation from ether at 185°, was isolated. The latter gave on analysis:

C = 82·94; H = 5·81; MeO = 6·93.

$C_{28}H_{21}O_2(MeO)$ requires C = 82·86; H = 5·71; MeO = 7·38 per cent.

The molecular weight, as determined in chloroform solution by the boiling point method, was 417 ($C_{29}H_{24}O_3$ requires 420).

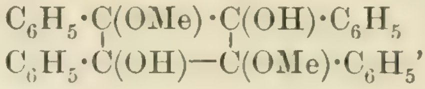
The compound had no action on Fehling's solution until hydrolysed by boiling with dilute acids. When boiled with excess of 20 per cent. hydrochloric acid it was converted into benzoin, benzoin methyl ether, and benzil. In addition, the compound was readily oxidised by alkaline potassium permanganate with the formation of benzil, benzoic acid, and an acid melting at 185—186°, which from its reactions appeared to be α-phenylcinnamic acid. These properties are in agreement with the idea that the compound under examination is produced by the union of a molecule of benzoin with one of benzoin methyl ether through loss of water.

Examination of the Product Melting at 285°.—This compound was characterised by great stability and by its sparing solubility in all ordinary solvents. Analysis gave the same figures as those calculated for benzoin methyl ether.

$C = 79{\cdot}69$; $H = 6{\cdot}24$; $MeO = 13{\cdot}05$.

$C_{15}H_{14}O_2$ requires $C = 79{\cdot}65$; $H = 6{\cdot}20$; $MeO = 13{\cdot}72$ per cent.

The molecular weight in chloroform solution was, however, 439, so that the formula becomes $C_{30}H_{28}O_4$ (molecular weight, 452). After boiling with concentrated hydrochloric acid for six hours, the substance was recovered unchanged. Prolonged boiling with excess of alkaline potassium permanganate solution gave benzil, benzoic acid, and a small quantity of an acid melting at 170°. As stated in the introduction, we believe the compound to have the constitution



$$\begin{array}{l} C_6H_5\cdot C(OMe)\cdot C(OH)\cdot C_6H_5 \\ \qquad\quad | \qquad\qquad\quad | \\ C_6H_5\cdot C(OH)-C(OMe)\cdot C_6H_5, \end{array}$$

but nevertheless we failed to obtain any indication of the presence of hydroxyl groups, as the compound was quite insoluble in acetic anhydride or acetyl chloride, and was recovered unchanged when treated with these reagents for several hours at 120°.

The mode of formation of these compounds seems to be obscure. The reacting substances must be perfectly dry, and, moreover, the presence of methyl alcohol appears to be necessary, as no result was obtained when solutions of equimolecular proportions of benzoin and benzoin methyl ether in other solvents were saturated with hydrogen chloride. Again, on passing the gas for several hours into a fused mixture of the two constituents at 140°, benzil was the only product, and on boiling a similar mixture with dilute sulphuric acid, dibenzoylstilbene was obtained (*Ber.*, 1877, **4**, 337) together with unchanged benzoin methyl ether.

Experiments, in which Fischer's method of methylation was applied to specimens of benzoin of varying purity, showed, however, that the presence of nitriles had considerable influence on the formation of the two condensation compounds. Benzoin, which had been crystallised six times from absolute methyl alcohol and which was quite free from nitrogen, yielded on methylation about 6 per cent. of the compound melting at 185° and only a trace of that melting at the higher temperature. The yield of both substances was materially increased by the use of a specimen of benzoin which contained traces of nitrogen, whilst in a duplicate experiment with crude benzoin, in which a considerable proportion of nitrogenous compounds was present, the yield of the substance melting at 285° was increased to 12 per cent., the proportion of the compound of lower melting point being reduced to 1 per cent. Further experiments, in which hydrogen chloride was passed into solutions of benzoin or benzoin methyl ether in methyl alcohol containing potassium cyanide, gave negative results, and the addition of benzaldehyde to the above mixtures did not increase the yield of the products appreciably. These experiments were, however, of some value as they showed that when pure benzoin methyl ether was used, the compound of higher melting point was alone produced, indicating that its formation is independent of the presence of benzoin.

Attempted Synthesis of the Enolic Form of Deoxybenzoin.

As already mentioned, experiments were made with the view of determining if deoxybenzoin could be obtained in an enolic form ; the latter would be identical with hydroxystilbene. Accordingly 70 grams of α-stilbene dibromide were converted into α-bromostilbene (*Ber.*, 1895, **28**, 2693), which was purified by distillation under reduced pressure, and attempts were made to replace the bromine atom by the hydroxyl group by the agency of silver hydroxide. It was found that, when dissolved in wet alcohol and agitated with silver oxide at 60° for several hours, the bromostilbene, on recovery, deposited a small crop of beautiful needles. Successive treatments with fresh silver hydroxide gave additional quantities of this substance, but in diminishing amount, and finally no more was obtained. When recrystallised from carbon tetrachloride the product melted at 115—120°. Analysis gave :

$C = 85{\cdot}17$; $H = 6{\cdot}18$.

$C_{14}H_{12}O$ requires $C = 85{\cdot}71$; $H = 6{\cdot}12$ per cent.

It is unlikely, however, that this substance was hydroxystilbene, produced by the action of silver hydroxide, as, if so, continued treatment with the reagent should have ultimately decomposed the whole of the bromostilbene. Aqueous potassium hydroxide (10 per cent.) was similarly without action on bromostilbene even on prolonged boiling or on heating for several hours at 160°, and when fused with the alkali in a sealed tube at 200° for three hours, tolane was produced.

A series of experiments on deoxybenzoin in which we endeavoured to detect derivatives of an enolic form also gave no positive results. When dissolved in methyl iodide and boiled with silver oxide for twenty hours, most of the substance was recovered unchanged contaminated with a little bidesyl. Lander (*loc. cit.*) obtained a similar result using ethyl iodide. The compound was also unaffected by heating to 100° with methyl alcohol containing hydrogen chloride.

In conclusion, we wish to express our thanks to the Carnegie Trust for a research grant in aid of the work, and also to Professor Purdie for much valuable advice.

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CXXXI.—*The Influence of Mercuric Iodide on the Formation of Sulphonium Iodides.*

By Thomas Percy Hilditch and Samuel Smiles.

Attention has already been drawn by one of us to the influence which mercuric iodide exerts on the formation of sulphonium iodides. It was shown (Trans., 1900, **77**, 163) that the speed of reaction between alkyl halide and sulphide is enormously increased if mercuric iodide be added to the reaction mixture. For example, the interaction of ethyl iodide and dimethyl sulphide in the presence of mercuric iodide is complete at atmospheric temperatures in fifteen minutes, the yield of the compound Me_2EtSI,HgI_2 being quantitative. On the other hand, the action between dimethyl sulphide and ethyl iodide alone is scarcely complete in three days.

In preparing compounds of the ammonium or sulphonium type which contain two or more different radicles, it is well known that the more complex alkyl groups are apt to be displaced by the simpler. This has led to erroneous conclusions with regard to the stereochemistry of sulphur and nitrogen. Kruger (*J. pr. Chem.*, 1876, [ii], **14**, 207) claimed that the product of the action between diethyl sulphide and methyl iodide was different from that yielded by methyl ethyl sulphide and ethyl iodide, and concluded that the four valencies of sulphur are not equal. Klinger and Maassen (*Annalen*, 1888, **243**, 193) repeated these experiments at atmospheric temperature and showed that the products of the two reactions are identical. Kruger's experiments were made at 100° and had led to impure products. More recently, Wedekind (*Ber.*, 1899, **32**, 517) stated that isomeric forms of phenylbenzylmethylallylammonium iodide are obtained according to whether benzylmethylaniline is treated with allyl iodide or benzylallylaniline with methyl iodide. Jones, however (Trans., 1905, **87**, 1721), has shown that the supposed isomeride derived from the latter reaction is really benzylphenyldimethylammonium iodide.

In the paper by one of us to which reference is made above, it was stated that the application of mercuric iodide in these reactions would probably be of use in obtaining sulphonium bases of high molecular weight, since the addition of alkyl iodide proceeds very rapidly and the reaction can be stopped at the initial stage before the secondary process of replacement has set in. The present paper deals with this question.

To illustrate the use of the reagent, we have chosen two sulphides containing groups which are known to be readily displaced by the action of methyl or ethyl iodides.

Ethyl Disulphide.—Saytzeff (*Zeitsch. für Chem.*, 1870, 108 and 256) treated ethyl disulphide with ethyl iodide at 100° and found that decomposition took place, triethylsulphonium iodide being formed with liberation of iodine. We have repeated this experiment at the atmospheric temperature with the same result. The action proceeds very slowly, there being no visible change in the mixture until two or three months have elapsed; triethylsulphonium iodide is then deposited and iodine is set free. From experiments which are described later, there can be no doubt that addition of ethyl iodide takes place according to the scheme:

$$C_2H_5{\cdot}S_2{\cdot}C_2H_5 + C_2H_5I = C_2H_5{\cdot}S_2(C_2H_5)_2I,$$

but the reaction takes place so slowly that before this product is formed in sufficient quantity to be isolated, it is decomposed by the excess of ethyl iodide, the thioethyl group, $S{\cdot}C_2H_5$, being replaced by ethyl.

If mercuric iodide be present the addition proceeds more rapidly, and by stopping the reaction at a suitable moment, we have succeeded in isolating the sulphonium iodide, $(C_2H_5)_3S_2I$, in the form of a mercuric iodide double salt. Prolonged interaction of the reagents yields triethylsulphonium iodide as $(C_2H_5)_3SI,HgI_2$ or $(C_2H_5)_3SI,2HgI_2$. The following comparison illustrates this.

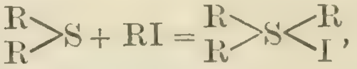
Reagents.	Approximate Times.	Chief Product.
Equimolecular proportions of		
$(C_2H_5)_2S_2$ and HgI_2	12 hours	$(C_2H_5)_3S_2I,2HgI_2$
with excess of C_2H_5I	3 days	$(C_2H_5)_3SI,2HgI_2$.

Dibenzyl Sulphide.—Cahours (*Ann. Chim. Phys.*, 1877, [v], **10**, 26) treated dibenzyl sulphide with methyl iodide at 100°. He isolated trimethylsulphonium and benzyl iodides as the chief products with small quantities of benzyldimethylsulphonium iodide. Schöller (*Ber.*, 1874, **7**, 1274) attempted to prepare dibenzylmethylsulphonium iodide from the same reagents at the atmospheric temperature, but he was only able to obtain the same products as Cahours at the higher temperature. We have found that in the presence of mercuric iodide the addition of methyl iodide to dibenzyl sulphide advances rapidly, and with care an almost theoretical yield of dibenzylmethylsulphonium mercuric iodide, $(C_7H_7)_2MeSI,HgI_2$, may be obtained. Dibenzylethylsulphonium iodide was prepared in the same way.

At present, we are not able to offer any well-founded explanation of this accelerating influence of mercuric iodide. It is, however, certain that the metallic salt forms, with the sulphides, additive products, R_2S,HgI_2 (Smiles, Trans., 1900, **77**, 163), and it is these substances and not the free sulphides which react with the alkyl iodide.

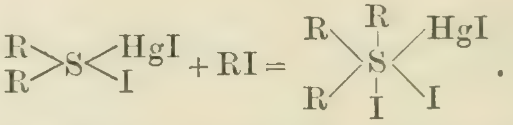
That the change of these sulphide-mercuric iodides to the sulphonium-mercuric iodides proceeds so much more rapidly than the passage of sulphide to sulphonium iodide seems to show that these metallic addition products are not merely molecular compounds.* If this were the case, it would be difficult to find reason for the difference in speed of the reactions.

On the other hand, if it be granted that sulphur assumes a higher valency in the sulphides and sulphonium salts when they are combined with mercuric halide, the explanation is obvious. In one case, the reaction would proceed with the change of bi- to quadri-valent sulphur:



$$\begin{matrix}R\\R\end{matrix}\!>\!S + RI = \begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}R\\I\end{matrix},$$

and, in the other, with the change of quadrivalent to sexavalent sulphur:



This explanation is offered as the simplest and most probable.

In conclusion, it may be mentioned that a certain amount of evidence has been collected to show that the sulphonium additive products contain sulphur in the sexavalent state (Dobbin and Masson, Trans., 1885, **47**, 56; Smiles, Trans., 1900, **77**, 161; W. J. Pope and Neville, Trans., 1902, **81**, 1097). Perhaps the most conclusive is that adduced by Pope and Neville, who showed that optically active methylethylphenacylthetine becomes inactive on conversion into the mercuric iodide or chloride compounds.

EXPERIMENTAL.

Ethyl Disulphide and Ethyl Iodide.

(a) *In Presence of Mercuric Iodide; Formation of Diethylthioethylsulphonium.*

Three times the calculated amount of ethyl iodide was added to an acetone solution of equimolecular proportions of ethyl disulphide and mercuric iodide. The mixture was set aside at the ordinary temperature for fourteen hours; it was then freed from excess of mercuric iodide by filtration, and the brown filtrate was precipitated with ether. The mass of crystals which were obtained were purified by reprecipitation:

0·1719 gave 0·0676 HgS. Hg = 33·90.

0·2438 ,, 0·0526 CO_2 and 0·0261 H_2O. C = 5·88; H = 1·19.

$C_6H_{15}I_5S_2Hg_2$ requires Hg = 33·73; C = 6·07; H = 1·26 per cent.

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* The term is employed in the usual sense.

Diethylthioethylsulphonium dimercuric iodide, $(C_2H_5)_3S_2I,2HgI_2$ crystallises from acetone in blunt needles which melt at 104°. A mixture of this substance with triethylsulphonium dimercuric iodide (m. p. 116°) melted indistinctly at about 90°.

(b) *Prolonged Action with Mercuric Iodide; Formation of Triethylsulphonium.*

The mixture in acetone of disulphide, mercuric iodide, and ethyl iodide in the same proportions as before was set aside for three days at the ordinary temperature. The deep brown liquid after being separated from mercuric iodide was mixed with ether. The precipitate, consisting of triethylsulphonium dimercuric iodide, $(C_2H_5)_3SI,2HgI_2$, melted at 111—112°, and after purification formed pale yellow leaflets of melting point 115—116°:

0·1960 gave 0·0463 CO_2 and 0·0232 H_2O. C = 6·44; H = 1·31.
$C_6H_{15}I_5SHg_2$ requires C = 6·24; H = 1·30 per cent.

A sample of triethylsulphonium dimercuric iodide (m.p. 116°) was prepared from triethylsulphonium iodide and mercuric iodide (Smiles, Trans., 1900, **77**, 166). A mixture of this with the above product melted also at 115—116°.

When the same experiment was performed without the use of acetone as a solvent, the reaction was found to be more complete.

Two mercuric iodide compounds were isolated; one of these melted at 110° and was found to be identical with the substance $(C_2H_5)_3SI,HgI_2$ described in a former paper (Smiles, *loc. cit.*). On analysis:

0·1806 gave 0·0583 HgS. Hg = 27·97.
0·1625 ,, 0·0620 CO_2 and 0·0297 H_2O. C = 10·40; H = 2·03.
$C_6H_{15}I_3SHg$ requires Hg = 28·57; C = 10·29; H = 2·14 per cent.

The other compound was richer in mercuric iodide and was identical with that, $[(C_2H_5)_3SI,2HgI_2]$, described in the former experiment.

Hence triethylsulphonium is formed by the prolonged interaction of diethyl sulphide, ethyl iodide, and mercuric iodide.

(c) *Without Mercuric Iodide; Formation of Triethylsulphonium.*

A mixture of ethyl disulphide with excess of ethyl iodide was set aside in a sealed vessel at the ordinary temperature in the absence of light. In about three months, the liquid turned faintly brown, and subsequently large oblong plates began to form on the sides of the vessel. After about three years, sufficient crystalline matter had collected; the vessel was then opened, and the solid was separated from the deeply-coloured mother liquor and oil which had formed. The crystals after purification with alcohol were colourless; they melted at 145—146° with decomposition:

0·1290 gave 0·1239 AgI. I = 51·92.

$C_6H_{15}IS$ requires I = 51·63 per cent.

The oil which had separated together with these crystals was also examined; it was found to contain triethylsulphonium. No other product was isolated.

Dibenzyl Sulphide and Alkyl Iodide.

(a) *With Mercuric Iodide and Methyl Iodide.*

Equimolecular proportions of dibenzyl sulphide and mercuric iodide were mixed with acetone. The greater portion* of the mercuric iodide dissolved forming dibenzyl sulphide mercuric iodide (Smiles, Trans., 1900, 77, 164). Excess of methyl iodide was then added, and the mixture, with occasional shaking, was allowed to remain at the ordinary temperature. In about fifteen minutes, the mercuric iodide had completely dissolved, and in another half hour the sulphonium mercuric iodide began to crystallise in rosettes of yellow needles. These were filtered by the aid of the pump and recrystallised from hot acetone:

0·2287 gave 0·1820 CO_2 and 0·0462 H_2O. C = 21·70; H = 2·25.
0·2522 " 0·2012 " " 0·0492 H_2O. C = 21·76; H = 2·17.
0·2832 " 0·0807 HgS. Hg = 24·39.
$C_{15}H_{17}I_3SHg$ requires C = 22·22; H = 2·10; Hg = 24·69 per cent.

A further quantity of the substance was obtained by precipitating the original acetone mother liquor with ether. *Dibenzylmethylsulphonium mercuric iodide*, $(C_7H_7)_2MeSI,HgI_2$, melts at 155° and is sparingly soluble in cold acetone.

(b) *With Mercuric Iodide and Ethyl Iodide.*

Dibenzylethylsulphonium iodide mercuric iodide was obtained in a manner precisely similar to that described in the case of the methyl derivative. The reaction proceeds more slowly than with methyl iodide, the mercuric iodide requiring two hours to dissolve completely. The sulphonium compound begins to separate in about five hours. It was recrystallised from acetone and analysed:

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* The action between $(C_7H_7)_2S$ and HgI_2 is not complete in solution at the ordinary temperature; the remainder of the mercuric iodide dissolves as the original equilibrium is destroyed by the conversion of $(C_7H_7)_2S,HgI_2$ into sulphonium salt.

0·2367 gave 0·2021 CO_2 and 0·0509 H_2O. C = 23·29 ; H = 2·39.
$C_{16}H_{19}I_3SHg$ requires C = 23·3 ; H = 2·31 per cent.

Dibenzylethylsulphonium iodide mercuric iodide is sparingly soluble in cold acetone ; by spontaneous evaporation of the solution it separates in large, yellow, six-sided plates which melt at 115°.

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CXXXII.—*The Decomposition of Mercurous and Silver Hyponitrites by Heat.*

By PRAFULLA CHANDRA RÂY and ATUL CHANDRA GAÑGULI.

IN order to investigate the action of heat on mercurous and silver hyponitrites, the salts were heated in a short length of combustion tube, as previously described (Trans., 1905, **87**, 180), a tube filled with glass beads moistened with aqueous potassium hydroxide being interposed between the heating tube and the Sprengel pump to absorb any nitrous fumes.

I. *Mercurous Hyponitrite.**

The salt began to decompose, although very slowly, at 80°, and, on further raising the temperature, assumed a black colour, eventually changing at 150° to reddish-yellow, at which point decomposition ceased. No further evolution of gas was observed on raising the temperature to 200°, and no nitrous fumes were at any time visible.

A. *Analysis of the Gases Evolved.*

The nitric oxide in the gaseous product was estimated by absorption in alkaline sodium sulphite (Divers, Trans., 1899, **75**, 82), in which nitrous oxide is practically insoluble (see p. 1402). The nitrous oxide in the residual gas, which was found to support combustion without appreciable diminution of volume, was estimated by absorption in cold water. A small residue of nitrogen always remained. The nitrogen absorbed as nitrite by the alkali hydroxide was also estimated.

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* Divers states (Trans., 1899, **75**, 120, 121) that "mercuric hyponitrite is decomposed by heat largely into mercuric oxide and nitrous oxide, but partly into metal and nitric oxide . . . . the decomposition of mercurous hyponitrite by heat resembles that of the mercuric salt, except that much more metal is produced, as is natural."

B. *Analysis of the Solid Residue.*

The residue consisted of mercury, part of which was deposited in the cooler parts as a mirror, and mercuric oxide; the latter, however, was always associated with distinct traces of mercurous nitrate, and considerable difficulty was experienced in determining its amount. When the residue was treated with dilute nitric acid in the cold, the mercuric oxide and mercurous nitrate were at once dissolved, leaving globules of mercury behind, but no concordant results could be obtained, the amount of mercurous mercury being disproportionately high. Treatment with dilute hydrochloric acid was equally unsatisfactory.

Hada has already shown (Trans., 1896, **69**, 1667) that in presence of finely-divided mercury, a considerable proportion of mercuric nitrate or chloride is reduced to the mercurous state. The best method of determining the amount of mercurous nitrate seemed to be to estimate the nitrogen by Dumas' method. In some cases, therefore, the decomposition tube was once more exhausted and heated to dull redness; the nitrous fumes evolved were absorbed in the alkali, and the gas which was collected was found to be pure oxygen.* The nitrogen which was absorbed by the alkali hydroxide, in the form of nitrate and nitrite, which represented the nitrogen of mercurous nitrate, was estimated. That the residue really contained mercurous and not mercuric nitrate was proved by subjecting it to repeated levigation. In this manner the minute globules of mercury were removed, and, on treatment with dilute hydrochloric acid, calomel was still obtained, whilst the filtrate gave mercuric mercury.

In one experiment, 0·399 gram of salt gave 1·7 c.c. of nitrogen, 8 c.c. of nitrous oxide, and 19·1 c.c. of nitric oxide; the nitrogen absorbed in the potassium hydroxide in the circulation tube as nitrite in the first stage was 0·79 c.c., and that absorbed in the second stage in the form of nitrate and nitrite, due to mercurous nitrate, was 1·7 c.c., the total moist nitrogen being 21·74 c.c., measured at 27° and 760 mm.; the percentage of nitrogen therefore amounts to 6·03, that required by theory being 6·09.

The results of the above and two more experiments in which 0·329 gram and 0·4335 gram of salt respectively were heated are given in the following table, the nitrogen in the different forms being given in percentages:

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* The amount of oxygen was found to correspond with the mercuric oxide formed in the several reactions given below.

No. of expt.	N_2 as such.	N_2 as N_2O.	N_2 as NO.	N_2 absorbed in KOH in both stages.	Total N_2.
I.	0·47	2·22	2·65	0·69	6·03
II.	0·54	2·59	2·44	0·61	6·18
III.	0·61	2·16	2·50	0·85	6·12

From the results recorded above, it is established that the main products of decomposition of mercurous hyponitrite are mercury and mercuric oxide, with nitric oxide and nitrous oxide; mercurous nitrate and nitrogen are formed in small quantities only, and are probably due to secondary actions. If the "oxylic" formula of the salt be accepted with the diazo-grouping (Divers, *loc. cit.*, 123), then, according to the usual decomposition of diazo-compounds, nitrogen should have formed the main product; in fact, Zorn's observation that ethyl hyponitrite breaks up into nitrogen and alcohol (and aldehyde) would lend support to this view. We should thus have expected the decomposition to proceed according to the following equation, the more so as mercuric oxide is a stable compound at 150—200°:

$$Hg{\cdot}O{\cdot}N{\vdots}N{\cdot}O{\cdot}Hg = 2HgO + N_2.$$

But as the amount of nitrogen actually obtained was very small, the "oxylic" structure alone does not seem satisfactorily to explain the experimental results. As, however, nearly half the amount of nitrogen of the salt appears as nitric oxide, a sort of tautomeric change seems to take place under the action of heat, and, roughly speaking, half the number of molecules retains the "oxylic" (yielding nitrous oxide) and the other half assumes the "imidic" structure (giving nitric oxide), thus:

$$Hg{\cdot}N{\vdots}O = Hg + NO \quad . \; . \; . \quad (1)$$
$$Hg{\cdot}O{\cdot}N{\vdots}N{\cdot}O{\cdot}Hg = [Hg_2O = Hg + HgO] + N_2O \quad . \; . \; . \quad (2).$$

This would bring the hyponitrite into close relationship with the corresponding nitrites (compare Rây and Gañguli, Proc., 1905, 21, 278).*

We have now to account for the formation of the small, but by no means negligible, quantity of mercurous nitrate. The reaction which readily suggests itself is

$$3(HgON)_2 = 2HgNO_3 + 4Hg + 2N_2.$$

But this equation is hardly admissible, as the amount of free nitrogen actually formed is equal to that existing in the mercurous nitrate (see Expt. I). Possibly the nitrate is the product of a more complex reaction, for example,

$$4(HgON)_2 = 2HgNO_3 + 6Hg + N_2 + 2N_2O.$$

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* The "imidic" constitution of mercury hyponitrites has already been hinted at (Trans., 1897, 71, 1104).

II. *Silver Hyponitrite.*

In view of the interesting results with mercurous hyponitrite, it seemed desirable to study further the action of heat on the silver analogue, although Divers has already described it (Trans., 1899, **75**, 108).

The substance, which was pale yellow, was washed and dried exactly as the corresponding mercury compound. The analyses of several distinct preparations are given below :

	I.	II.	III.	IV.	Theory.
Ag......	77·81	78·50	77·37	77·23	78·26
N	10·78	—	—	—	10·15

It will be seen that the percentage of silver is slightly lower, whilst that of nitrogen is correspondingly higher, than the theoretical amounts. This appears to be due to the fact that traces of alkali, including sodium nitrite and hyponitrite, are carried down with the precipitate. The method of heating was precisely the same as in the preceding instance.* We shall therefore confine ourselves to giving only the results of a few typical experiments. The gases evolved were as in the case of the preceding compound nitrogen, nitrous oxide, and nitric oxide, but nitrous fumes were also distinctly perceptible. The solid residue consisted of a white mass of metallic silver with a small amount of silver nitrate. The following table shows the percentage yield of each of these compounds :

Exp.	N as NO.	N as N_2O.	N as such.	N absorbed in the KHO.	N in $AgNO_3$.	Total.
I.	6·38	1·02	1·11	1·44	0·35	10·30
II.	6·77	1·28	1·01	1·08	0·35	10·49

The percentage of silver obtained in the metallic state and also as nitrate was :

	As free silver.	As nitrate.	Total.
I.	74·49	2·74	77·23
II.	74·55	2·68	77·23

It will be seen that the decomposition products of silver and mercurous hyponitrites are similar in many respects. The only difference is that in the former case nitrogen monoxide is formed in much smaller quantity ; indeed, after the absorption of nitric oxide by alkaline sodium sulphite solution,† the residual gas, which is made up of almost equal volumes of nitrogen monoxide and nitrogen, did not support the combustion of phosphorus. A comparative study of the effect of heat on the two compounds helps us to understand the mechanism of the reactions. What actually happens seems to be as follows:

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* The salt began to decompose very slowly at 100°, and at 140° the evolution of the gas was brisk.

† About 1·5 to 2 c.c. of a solution of sodium sulphite was used for this purpose, and it was proved that it was almost without appreciable solvent action on nitrogen monoxide.

$$\begin{aligned} 2(Ag{\cdot}O{\cdot}N)_2 &= 2[Ag_2O] + 2N_2O \quad . \; . \; . \; (1). \\ &= 2Ag_2 + O_2 + 2N_2O \end{aligned}$$

$$(Ag{\cdot}N{\cdot}O)_2 = Ag_2 + 2NO \quad . \; . \; . \; (2).$$

$$2NO + O = N_2O_3 \quad . \; . \; . \; (3).$$

$$2N_2O_3 + Ag = 2(NO{\cdot}NO_2) + Ag = AgNO_3 + 3NO \quad . \; . \; . \; (4).$$

In the case of mercurous hyponitrite the proportion of "oxylic" to "imidic" molecules was nearly equal, whereas in the present instance by far the larger number of molecules is "imidic"; moreover, as silver oxide is unstable towards heat, its existence is only hypothetical. What we really get is silver and oxygen. The formation of nitrous fumes is thus easily accounted for.* A part of the nitrogen trioxide or, if its existence at a high temperature be denied, the nitrogen peroxide which it yields (and which may be looked upon as nitrosyl nitrate) acts on silver and yields silver nitrate.

The nitrous fumes, however, would be absorbed by the potassium hydroxide (Rây and Gañguli, Proc., 1905, 21, 279).

The production of nitrogen has yet to be explained. It is quite possible that a portion of the salt decomposes in the following way:

$$5AgNO = AgNO_3 + \left\{ \begin{matrix} 2Ag_2O \\ 4Ag + 2O \end{matrix} \right\} + 2N_2 \quad . \; . \; . \; (5).\dagger$$

Silver nitrate is formed, according to our view, in conformity with equations (4) and (5); in the table given above, the ratio of nitrogen in the total silver nitrate and that in the free state is nearly as 1 : 3; if the silver nitrate according to equation (4) be left out of account, the above ratio will probably come out as 1 : 4, as demanded by equation (5).

The formation of nitrogen according to the equation: $3(AgON)_2 = 4Ag + 2AgNO_3 + 2N_2$ is not borne out by the analytical data given above.

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* The occurrence of nitrous fumes, according to our view, is due only to a secondary reaction, whilst Divers (*loc. cit.*, p. 110) and Kirschner (*Zeitsch. anorg. Chem.*, 1898, **16**, 424) regard it as a direct product of heating the salt. Divers also looks on the nitric oxide as the result of a series of complex reactions. It should be noted that these chemists conducted their experiments in quite a different manner, which introduced complications.

† In our next paper we hope to prove that hyponitrous acid breaks up mainly according to the equation: $5HNO = HNO_3 + 2H_2O + 2N_2$.

CXXXIII.—*Mercurous Hyponitrite.*

By PRAFULLA CHANDRA RÂY.

MERCUROUS hyponitrite, which has already been obtained in a somewhat impure condition by the author (Trans., 1897, **71**, 348), may be prepared (*a*) by precipitating mercurous nitrate with carefully neutralised sodium hyponitrite made according to Divers' method (Trans., 1899, **75**, 96, 119), (*b*) by precipitating mercuroso-mercuric nitrite (Rây, Trans., 1902, **81**, 644) with the crude alkaline hyponitrite, or (*c*) by precipitating mercurous nitrate with acid potassium hyponitrite (Thum, *Inaug. Dissert.*, 1893). The neutralisation of the alkali in the first case is of importance, as, if mercurous nitrate be employed, the hyponitrite is contaminated with mercurous oxide, whereas with the nitrite, as in the case of silver hyponitrite, no oxide is precipitated. A similar difference is observable in the action of mercuric nitrate and nitrite with sodium sulphate, the former alone yielding a precipitate of basic sulphate (Rây, Trans., 1897, **71**, 1103).

Mercurous hyponitrite prepared by the first two methods was washed by the aid of the pump and dried over sulphuric acid under diminished pressure. The salt has a bright yellow colour, that obtained from mercurous nitrate being usually more compact and deeper in tint. Like the corresponding silver salt, it dissolves readily in dilute nitric acid, and can be precipitated from the solution by cautious addition of sodium carbonate. There is, however, one important difference. The nitric acid solution of mercurous hyponitrite immediately becomes opalescent from separation of mercury, which remains at first in a fine state of suspension; if, however, the solution be set aside for an hour or so, the mercury settles at the bottom and a slow and continuous effervescence takes place owing to the liberation of nitrogen monoxide. This phenomenon, which was overlooked by Thum, takes place equally with strong nitric acid, but in the latter case, if the solution is heated to boiling, it becomes quite clear, as the separated mercury quickly dissolves. The dissociation occurs even if ice-cold acid is used.

Mercurous hyponitrite in acid solution thus undergoes partial dissociation according to the equation:

$$Hg_2N_2O_2 = Hg + Hg(NO_2)_2.$$

Analyses of different preparations are given below:

	I.	II.	III.	IV.	Calculated.
Hg	84·76	84·16	85·38	86·92	86·96
N	6·12	—	—	—	6·09

No. IV. represents the purest sample which could be prepared. The mercury was weighed as sulphide. On evaporation of the filtrate, about 1 per cent. of alkali, estimated as sodium sulphate, was usually obtained. It is well known that whenever mercuric oxide is prepared by treating mercuric nitrate with alkali hydroxides, it is contaminated not only with alkali but also with traces of nitrate, however carefully it may be washed (see Trans., 1897, 71, 1100). In the above preparations, if the alkaline impurities are allowed for, the percentages of mercury more closely approach the theoretical amount.

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CXXXIV.—*Cupric Nitrite.*

By PRAFULLA CHANDRA RÂY.

A SOLUTION of cupric nitrite can be prepared in a pure state by double decomposition between (*a*) cupric sulphate and barium nitrite or (*b*) cupric chloride and silver nitrite. The solution obtained in this way has a bright grass-green colour. According to Hampe, it evolves nitric oxide even in the cold (*Annalen*, 1863, 125, 345), whilst Berzelius states that it absorbs oxygen from the air and is slowly converted into nitrate. Hampe also describes a basic nitrite of the formula $Cu(NO_2)_2,CuO,xH_2O$, formed by evaporation of this solution. In continuation of my study of the nitrites it seemed desirable to bring cupric nitrite within its scope.

Preliminary experiments confirmed the above statements, and showed that a dilute solution of cupric nitrite is slowly oxidised by absorption of atmospheric oxygen, but that when evaporated over sulphuric acid, even under diminished pressure, it undergoes autoxidation, liberating nitric oxide.

I. *Atmospheric Oxidation.*

An approximately 8·5 per cent. solution of cupric nitrite was kept in a stoppered bottle, the total nitrogen being determined from time to time by the Crum-Frankland method, whilst that as nitrite was estimated by the "urea" process; portions of 2 c.c. were usually withdrawn for this purpose. If the solution had remained unchanged, the nitrogen obtained by these two methods would have been identical; but it was found that whilst the total nitrogen remained constant, that given by the "urea" method diminished from day to day. The nitrite thus absorbed oxygen from the air, and a change was further indicated by a gradual alteration in colour from pale green to bluish-green. Under the conditions of the experiment, the reaction was evidently between the copper nitrite and the oxygen of the dissolved air, the supply of which was renewed as the stopper was opened from time to time. Assuming that the concentration of dissolved oxygen remains constant throughout the course of the experiment, which may well be the case if the temperature be fairly constant, the reaction is apparently unimolecular, the results, except in the early stages, being concordant with theory.

Experiment I.—Two c.c. solution = 12·4 c.c. NO, temperature (atmospheric) approximately 15 – 10°.

No. of days.	C.c. of nitrogen by the "urea" method $= a - x$.	$1/t \log a/a - x = K$.
0	12·4	—
2	12·0	0·00712
13	11·0	0·0040
18	10·5	0·0040
27	9·6	0·0041
38	9·0	0·0039
57	7·5	0·0039

The results of another experiment with an approximately 3·2 per cent. solution are tabulated below.

Experiment II.—Two c.c. solution = 4·6 c.c. NO; temperature, 31 – 29°.*

No. of days.	C.c. of nitrogen by the "urea" method $= a - x$.	$1/t \log a/a - x = K$.
0	4·6	—
3	4·5	0·0032
6	4·1	0·0083
7	4·0	0·0086
10	3·8	0·0082

The disturbing effects during the initial stages of the reaction are very marked in both experiments, but if a sufficiently wide interval of time is chosen the constancy is unmistakable.

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* This experiment was made at Calcutta. I am indebted to Mr. Bidhubhusan Dutt, M.A., Assistant, Chemical Department, for calculating the values of *K* from my experiments.

II. *Autoxidation.*

When a solution of cupric nitrite was evaporated under diminished pressure over sulphuric acid, nitric oxide was invariably evolved; the residue, which was insoluble in water, was bluish-green, and its surface was pierced with holes, showing that the disengagement of gas was most rapid in the semi-solid stage. As the nitric oxide was no doubt liberated according to the equation:

$$3Cu(NO_2)_2 = Cu(NO_3)_2 + 2CuO + 4NO,$$

it was to be expected that the residue would contain both nitrite and nitrate; it was therefore finely powdered and boiled with aqueous sodium hydroxide in order to eliminate the copper, the ratio of nitritic to nitratic nitrogen in the filtrate being determined as recorded below. It has already been shown that a solution of alkaline nitrites can be safely evaporated even at the boiling temperature without decomposition or oxidation (Trans., 1904, 87, 179).

No. of expt.	$\dfrac{\text{Nitritic nitrogen}}{\text{Nitratic nitrogen}}$
I.	7·0
II.	1·0
III.	0·33

The substance was thus invariably a mixture of nitrite and nitrate, and the formulæ hitherto assigned to the copper nitrites require revision. The nearest approach to a basic nitrite, $Cu(NO_2)_2,CuO$, was in experiment I, where the ratio of Cu : N was 1·8 : 1; but even here the contamination with basic nitrate vitiated the calculation, as $12\frac{1}{2}$ per cent. of the total nitrogen was nitratic. In my previous papers (Trans., 1904, 85, 523; 1905, 87, 177) I have shown that in Group II of the periodic system, besides the metals of the alkaline earths, magnesium and bivalent mercury also yield normal nitrites (*loc. cit.*, p. 180). The position of copper, however, is not sharply defined, and as a member of the eighth or transitional group it is quite natural to expect that its nitrite should be unstable.

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* This investigation was carried on at the above place towards the end of 1904. My abrupt departure from England and pressure of work in other directions have delayed publication.

CXXXV.—*Researches on Morphine. Part III.*

By **Frederic Herbert Lees.**

It was shown by Schryver and Lees (Trans., 1900, **77**, 1024, and 1901, **79**, 563) that by the interaction of morphine, and either phosphorus trichloride, phosphorus tribromide or hydrobromic acid, and of codeine and phosphorus tribromide, the alcoholic hydroxyl group of the respective base is replaced by chlorine or bromine. The crystalline bases, chloromorphide, $C_{17}H_{18}O_2NCl$, bromomorphide, $C_{17}H_{18}O_2NBr$, and bromocodeide, $C_{18}H_{20}O_2NBr$, were obtained in this way.

Many years previously, a crystalline base, chlorocodeide, $C_{18}H_{20}O_2NCl$, was described by Vongerichten (*Annalen*, 1881, **210**, 107), who obtained it by the interaction of codeine and phosphorus pentachloride.

More recently it has been shown by Pschorr (*Ber.*, 1906, **39**, 3130) that chloromorphide is also produced by the action of anhydrous liquid hydrogen chloride on morphine.

It was, furthermore, demonstrated by Schryver and Lees (*loc. cit.*) that when chloromorphide, bromomorphide, and bromocodeide are hydrolysed with water, morphine and codeine are not simply regenerated, but in each case at least two bases isomeric, but not identical, with morphine and codeine respectively are produced.

The products isolated by Schryver and Lees from the hydrolysis of these halogen derivatives can be represented as follows:

$$\begin{tikzcd}
 & \text{Hydrochloride } [\alpha]_D - 92{\cdot}5^\circ. \\
\text{Chloromorphide} \arrow[ur] \arrow[dr] & \\
 & \beta\text{-}\textit{iso}\text{Morphine} \\
\text{Bromomorphide} \arrow[ur] \arrow[dr] & \\
 & \textit{iso}\text{Morphine}
\end{tikzcd}$$

$$\text{Bromocodeide} \longrightarrow \textit{iso}\text{Codeine}.$$

Of these isomeric bases, *iso*morphine was more fully studied by Schryver and Lees (*loc. cit.*), particularly with respect to its behaviour on exhaustive methylation as compared with that of morphine.

It has since been shown by Vongerichten (*Ber.*, 1903, **36**, 159) and independently by Knorr and Hörlein (*Ber.*, 1906, **39**, 4409) that chlorocodeide on hydrolysis yields an isomeride of codeine melting at 180° and having $[\alpha]_D$ −94° in ethyl alcohol. These investigators found this base to be identical with the so-called "*pseudo*codeine" which was first obtained by Merck (*Arch. Pharm.*, 1891, **229**, 161) by the action of dilute sulphuric acid on codeine.

The further investigation of the halogen derivatives of morphine and codeine and the products of their hydrolysis has been in progress by the author for some considerable time, and the further results obtained form the subject of the present paper.

When chloromorphide is methylated by means of sodium ethoxide and dimethyl sulphate, chlorocodeide, identical with the product of the interaction of phosphorus pentachloride and codeine, is produced. The same substance can also be prepared in good yield by the interaction of phosphorus trichloride and codeine.

When bromomorphide is methylated in a similar manner, bromocodeide is produced.

It is thus proved that chlorocodeide and bromocodeide are simply the codeine analogues or methyl ethers respectively of the corresponding morphides.

It seemed of importance to settle this point in view of the different conditions under which the morphides and codeides have been prepared.

By the hydrolysis of chloromorphide, the author has isolated, besides *β-iso*morphine, an hitherto undescribed isomeride of morphine. On methylation, it yields the codeine analogue which is in all respects identical with the above-mentioned "*pseudo*codeine."

As pointed out by Knorr and Hörlein (*Ber.*, 1906, 39, 4409), the name "*pseudo*codeine" was not happily chosen by Merck for his base, since it is not the methyl ether of the base known as *pseudo*morphine, which is an oxidation product of the formula $C_{34}H_{36}O_6N_2$. The position becomes more unfortunate, however, now that the morphine analogue of "*pseudo*codeine" has been isolated, inasmuch as the new base cannot, of course, be termed "*pseudo*morphine," which is the name of a well-known base which has been fully characterised by means of a large number of derivatives.

It has therefore been decided to designate the new base from chloromorphide *neo*iso*morphine*, and the author proposes the adoption of *neo*iso*codeine* for the methyl ether to replace "*pseudo*codeine," which is a decided misnomer as applied to this base.

*Neo*iso*morphine*, $C_{17}H_{19}O_3N$, forms brilliant, prismatic needles from ethyl alcohol. These contain one molecule of alcohol of crystallisation and melt at 278°. The *hydrochloride*, $C_{17}H_{19}O_3N,HCl$, has $[\alpha]_D$ $-79\cdot1°$ in aqueous solution; the *methiodide*, $C_{17}H_{19}O_3N,MeI$, melts at 297° and has $[\alpha]_D$ $-54\cdot5°$ in aqueous solution.

*Neo*iso*codeine*, $C_{18}H_{21}O_3N$, obtained by the methylation of neo*iso*morphine, forms large, colourless prisms from ethyl acetate, which melt at 181—182° and have $[\alpha]_D$ $-96\cdot6°$ in ethyl alcohol.

In a preliminary communication (Proc., 1906, 22, 253), the author in conjunction with F. Tutin has already announced some results obtained from the hydrolysis of bromocodeide with water. It was shown that by fractional crystallisation of the mixture of bases produced, two definite substances were obtained:

A-Base.—This formed slender, prismatic needles melting at 147—147·5° and had $[\alpha]_D$ $-205°$ in chloroform.

B-Base.—This formed colourless, tabular prisms melting at 171—172° and had $[\alpha]_D$ $-155°$ in chloroform.

The latter was shown to be iso*codeine*, the codeine analogue of *iso*morphine which is the chief product of the hydrolysis of bromomorphide, for when *iso*morphine is methylated, a base identical with the *B*-base is quantitatively produced.

The *A*-base has now been definitely proved to represent a molecular mixture of *iso*codeine and β-iso*codeine,* the codeine analogue of β *iso*morphine which is formed together with *iso*morphine and neo*iso*morphine respectively by the hydrolysis of bromo- and chloro-morphide.

The composition of the *A*-base was determined by the fact that it was produced by crystallising from ethyl acetate a mixture of equal parts of *iso*codeine and β-*iso*codeine, which were prepared by the methylation of *iso*morphine and β-*iso*morphine respectively, as also by the fact that its methiodide was resolved into *iso*codeine methiodide (m. p. 270°; $[\alpha]_D$ $-103·3°$ in water); methyl *iso*morphimethine (m. p. 168—169°), and β-*iso*codeine methiodide (m. p. 215—216°; $[\alpha]_D$ $-140·2°$ in water).

It must be noted that the *iso*codeine (m. p. 144°; $[\alpha]_D$ $-169°$) obtained by Schryver and Lees (*loc. cit.*) by the action of water on bromocodeide was not pure and must have contained a small proportion of β-*iso*codeine. The methiodide of this base was, however, purified by recrystallisation, the purified salt being in all respects identical with *iso*codeine methiodide prepared by two independent methods of methylation from pure *iso*morphine (from bromomorphide; m. p. 247°; $[\alpha]_D$ $-166·5°$). The methiodides produced by the three methods had the same melting point and specific rotatory power, and each specimen afforded methyl *iso*morphimethine (m. p. 167°).

Although the fact that a mixture of bases is the direct result of the hydrolysis of bromocodeide with water was published by Lees and Tutin (*loc. cit.*) in November of last year, Knorr and Hörlein had apparently not seen the publication, for they have recently (*Ber.*, 1907, 40, 2032) based important conclusions respecting the isomerism of codeine, *iso*codeine, and neo*iso*codeine upon the products of the oxidation of these bases when they were obviously unaware that the *iso*codeine of Schryver and Lees (m. p. 144°), which they apparently oxidised, had in the meantime been shown to consist of a mixture of two isomeric bases only one of which is *iso*codeine.*

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* See Addendum.

β-iso*Codeine*, $C_{18}H_{21}O_3N$, produced by the methylation of β-*iso*morphine, is a syrupy base which did not crystallise. Its *methiodide*, $C_{18}H_{21}O_3N,MeI$, however, forms small, glistening, tabular crystals from water (m. p. 215—216°; $[\alpha]_D$ $-145.5°$ in water).

When an aqueous solution of β-*iso*codeine methiodide is boiled with dilute sodium hydroxide, it is converted into a *methine* base which is an almost colourless oil. This methine base forms a *methiodide* which is readily soluble in alcohol or water, and was not further investigated on account of lack of sufficient material.

The relation between the halogen derivative of morphine and codeine and the bases isolated by their hydrolysis can be now represented as follows:

$$\begin{tikzcd}
\beta\text{-}\textit{iso}\text{Morphine} \arrow[d] & \text{Chloromorphide} \arrow[l] \arrow[r] \arrow[d] & \text{Neo}\textit{iso}\text{morphine} \arrow[d] \\
\begin{array}{c}\beta\text{-}\textit{iso}\text{Codeine} \\ \text{(not yet isolated} \\ \text{from chlorocodeide)}\end{array} & \text{Chlorocodeide} \arrow[l] \arrow[r] & \text{Neo}\textit{iso}\text{codeine} \\
\beta\text{-}\textit{iso}\text{Morphine} \arrow[d] & \text{Bromomorphide} \arrow[l] \arrow[r] \arrow[d] & \textit{iso}\text{Morphine} \arrow[d] \\
\beta\text{-}\textit{iso}\text{Codeine} & \text{Bromocodeide} \arrow[l] \arrow[r] & \textit{iso}\text{Codeine.}
\end{tikzcd}$$

With regard to the relationship of these bases, respectively, to morphine and codeine, the view expressed by Lees and Tutin (*loc. cit.*) that they were optically isomeric with the latter bases was based upon the fact that, besides *iso*codeine and β-*iso*codeine, codeine was also isolated from the hydrolysis of the entire crude product of the interaction of codeine and phosphorus tribromide. Further experiment has shown that this fact does not justify the conclusion arrived at, since the codeine was most probably derived from a codeine ester of phosphorous acid and not from an optically isomeric bromocodeide. Further study of these substances on the lines now being followed by Knorr cannot fail to elucidate the question of the relations of these bases to each other and to morphine and codeine

EXPERIMENTAL.

Methylation of Chloromorphide. Formation of Chlorocodeide.

Chloromorphide was methylated in the usual manner with sodium ethoxide and dimethyl sulphate in alcoholic solution. On cooling, the methylated product separated together with the sodium methyl sulphate formed in the reaction. The crystalline material was collected, washed with water, dried by absorption, and recrystallised from ethyl alcohol. Glistening leaflets were thus obtained melting at 152—153°:

0·3095 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D $-9.42°$, whence $[\alpha]_D$ $-380.4°$.

Chlorocodeide, prepared by the interaction of codeine and phosphorus pentachloride according to the conditions given by Vongerichten (*loc. cit.*), melted at 152—153°, and

0·2705 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D $-8·25°$, whence $[\alpha]_D$ $-381·2°$.

When the substances prepared by the two methods were intimately mixed, the melting point was not changed.

Action of Phosphorus Trichloride on Codeine. Formation of Chlorocodeide.

The reaction between phosphorus trichloride and codeine in chloroform solution results chiefly in the formation of uncrystallisable codeine esters of phosphorous acid, and very little chlorocodeide is produced, even when the mixture is boiled for several hours. When, however, dry codeine was saturated with excess of phosphorus trichloride, the mixture heated for two hours on a water-bath, the product dissolved in alcohol, poured into water, made alkaline with sodium carbonate, and extracted with chloroform, a good yield of the chloro-base was obtained. After recrystallisation from ethyl alcohol it melted at 152—153°, and

0·3265 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D $-9·90°$, whence $[\alpha]_D$ $-379°$.

An intimate mixture of this base and that prepared by other methods showed no change in the melting point.

Methylation of Bromomorphide. Formation of Bromocodeide.

Bromomorphide was methylated in the same manner as was chloromorphide. The methylated base, which crystallised from the alcoholic solution, was freed from sodium methyl sulphate by washing with water, dried on porous earthenware, and recrystallised from ethyl alcohol. It separated as glistening, prismatic crystals, which melted at 161—162°, and this melting point was not affected by admixture with bromocodeide prepared directly from codeine:

0·4890 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D $+1·90°$, whence $[\alpha]_D$ $+48·6°$.

A specimen of bromocodeide, prepared by the interaction of phosphorus tribromide and codeine, had the following specific rotatory power:

0·5261 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D $+2·00°$, whence $[\alpha]_D$ $+47·5°$.

*Hydrolysis of Chloromorphide. Formation of β-*iso*Morphine and Neo*iso*morphine,* $C_{17}H_{19}O_3N$.

Chloromorphide (39 grams) was suspended in two equal portions in water (150 c.c. in each case). The mixture was then heated on a water-bath, and acetic acid gradually added until solution of the base was effected, when the solutions were then vigorously boiled for three hours in a reflux apparatus. The whole of the pale yellow, aqueous product was then concentrated on a water-bath to a syrup to which alcohol was added repeatedly, followed by continued evaporation. After a time a crystalline salt began to separate from the alcoholic solution, and on standing overnight several grams of this had collected. The crystalline salt was separated from the dark coloured mother-liquor, and on washing with alcohol was obtained quite white. It was found to be only sparingly soluble even in warm water, and was easily purified by recrystallisation from this solvent. The base was isolated from this salt by dissolving in warm water, adding excess of sodium carbonate, and extracting several times with chloroform. The residue from the chloroform solution was a faintly yellow, viscous syrup which was dissolved in warm alcohol. Almost immediately the base separated in the form of beautiful glistening, colourless, prismatic crystals.

This base was readily identified as *β-iso*morphine. It melted at 183—184° and exhibited the characteristic behaviour on heating previously recorded by Schryver and Lees (*loc. cit.*), and also contained one-half a molecule of alcohol of crystallisation:

1·0353 of the air-dried base lost 0·0815 at 110°. $C_2H_6O = 7{\cdot}87$.

$(C_{17}H_{19}O_3N)_2,C_2H_6O$ requires $C_2H_6O = 7{\cdot}47$ per cent.

*Isolation of Neo*iso*morphine,* $C_{17}H_{19}O_3N$.—The alcoholic mother-liquor from the *β-iso*morphine hydrochloride was further concentrated, and on long standing in a desiccator deposited 13 grams of crystalline salt, which was insoluble in alcohol, and was therefore easily obtained free from the dark coloured mother-liquor by washing. This further fraction of hydrochloride was, unlike the *β-iso*morphine hydrochloride, excessively soluble in water:

0·4898 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube α_D $-3{\cdot}94°$, whence $[\alpha]_D$ $-100{\cdot}5°$.

*β-iso*Morphine hydrochloride has the specific rotatory power $[\alpha]_D$ $-200{\cdot}8°$.

It was thus apparent that the second fraction of hydrochloride contained a new base.

It was found that the most convenient means of obtaining the base from the hydrochloride is to add, cautiously, dilute ammonia solution to the aqueous solution of the salt, when the base is precipitated and on stirring becomes crystalline. The crystalline base was collected, washed with water, dried on porous earthenware, and recrystallised from hot ethyl alcohol. It is only very sparingly soluble in this solvent, and a very large amount of the latter was required to effect solution. On concentrating the solution and allowing it to cool undisturbed, the base separated in the form of brilliant, prismatic needles.

Neoisomorphine melts at 278°, and crystallises from alcohol with one molecule of alcohol of crystallisation:

0·8820 of the air-dried base lost at 110° 0·1180. $C_2H_6O = 13·4$.
0·6700 „ „ „ „ „ 0·0895. $C_2H_6O = 13·4$.
$C_{17}H_{19}O_3N·C_2H_6O$ requires $C_2H_6O = 13·9$ per cent.

0·1672 of the dry base gave 0·4385 CO_2 and 0·1006 H_2O. C = 71·5; H = 6·7.

$C_{17}H_{19}O_3N$ requires C = 71·6; H = 6·7 per cent.

It was not possible to determine the specific rotatory power of neo*iso*morphine because of its exceedingly sparing solubility in all organic solvents.

The *hydrochloride* was, however, suitable for the purpose. It was prepared by dissolving the pure base in the theoretical amount of dilute hydrochloric acid and evaporating the solution repeatedly with alcohol. In this way the salt was obtained crystalline and anhydrous, for its weight remained constant on heating at 110°. It did not melt at or below 280°:

0·4600 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube α_D $-2·91°$, whence $[\alpha]_D$ $-79·1°$.

Neoisomorphine hydrochloride is extremely readily soluble in water, differing markedly in this respect from the hydrochlorides of morphine, *iso*morphine, and *β-iso*morphine.

The *methiodide* separates almost completely from alcohol on gentle warming of the solution of the base with methyl iodide as hard, glistening crystals which melt at 297°:

0·2219 gave 0·4130 CO_2 and 0·1038 H_2O. C = 50·8; H = 5·2.

$C_{18}H_{22}O_3NI$ requires C = 50·6; H = 5·1 per cent.

0·3900 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube α_D $-1·70°$, whence $[\alpha]_D$ $-54·5°$.

Methylation of Neoisomorphine. Formation of Neoisocodeine, $C_{18}H_{21}O_3N$.

Neo*iso*morphine (2 grams) was added to a solution of sodium (0·162 gram) in alcohol (20 c.c.), when the base readily passed into solution. A solution of dimethyl sulphate (1 gram) in alcohol was then added and the mixture gently warmed for five minutes. The solution was then poured into water, a slight excess of sodium hydroxide added, and the methylated base removed by extraction with chloroform. The residue from the chloroform quickly became crystalline. It was recrystallised from ethyl acetate, when it separated in large, colourless prisms, which melted at 181—182°, and this melting point was not altered by further crystallisation :

0·1281 gave 0·3395 CO_2 and 0·0810 H_2O. C = 72·3 ; H = 7·0.

$C_{18}H_{21}O_3N$ requires C = 72·4 ; H = 7·0 per cent.

0·3530 dissolved in ethyl alcohol and made up to 10 c.c. gave in a 1-dcm. tube α_D − 3·41°, whence $[\alpha]_D$ − 96·6°.

*Methylation of β-*iso*Morphine. Formation of β-*iso*Codeine*, $C_{18}H_{21}O_3N$.

*β-iso*Codeine was produced from *β-iso*morphine in the same manner as neo*iso*codeine was prepared from neo*iso*morphine. On removing the chloroform it was obtained as a clear syrup which did not crystallise during the time that could be spared to allow it to stand. It was analysed in the form of the molecular compound which it forms with *iso*codeine (p. 1416).

The *methiodide* was obtained as glistening crystals from alcohol. On recrystallisation from water it formed glistening, tabular prisms which melted at 215—216° without decomposition :

0·0730 gave 0·1365 CO_2 and 0·0390 H_2O. C = 51·0 ; H = 5·9.

$C_{19}H_{24}O_3NI$ requires C = 51·7 ; H = 5·4 per cent.

0·1503 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube α_D − 1·75°, whence $[\alpha]_D$ − 145·5°.

Methylation of iso*Morphine. Formation of* iso*Codeine*, $C_{18}H_{21}O_3N$.

iso*Codeine* was prepared from *iso*morphine in the manner described above. On removing the chloroform, the base formed a hard, crystalline mass, which on recrystallisation from ethyl acetate separated as large, colourless, tabular prisms which melted at 171—172° :

0·1386 gave 0·3670 CO_2 and 0·0865 H_2O. C = 72·2 ; H = 6·9.

$C_{18}H_{21}O_3N$ requires C = 72·4 ; H = 7·0 per cent.

0·4690 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube α_D − 5·65°, whence $[\alpha]_D$ − 150·6°.

Hydrolysis of Bromocodeide. Formation of iso*Codeine and β-*iso*Codeine.*

Bromocodeide (m. p. 162°) (20 grams) was suspended in water (150 c.c.) and just sufficient acetic acid added to effect solution of the base. The liquid was then vigorously boiled for four hours in a reflux apparatus, cooled, treated with excess of sodium carbonate, and the liberated base extracted with chloroform. The chloroform was removed and the syrupy base dissolved in warm ethyl acetate. The crystals which soon separated from the solution were observed to constitute a mixture of substances. By means of a prolonged series of fractional crystallisations from ethyl acetate, two substances were obtained the melting points and specific rotatory powers of which were unchanged by further crystallisation either from ethyl acetate or alcohol. These substances were as follows:

(*a*) A base, $C_{18}H_{21}O_3N$, which formed colourless prisms melting at 171—172°:

0·1935 dissolved in chloroform and made up to 10 c.c. gave in a 1-dcm. tube $a_D - 3·0°$, whence $[a]_D - 155°$.

This base was thus identical with *iso*codeine, and, moreover, its melting point remained unchanged on admixture with the base prepared by the methylation of *iso*morphine. It was also further identified by conversion through the methiodide (m. p. 270°; $[a]_D$ − 99°) into methyl *iso*morphimethine which melted at 168—169°.

(*b*) A base, $C_{18}H_{21}O_3N$, which formed slender, glistening, prismatic needles from ethyl acetate and melting at 147—147·5°:

0·1491 gave 0·3957 CO_2 and 0·0953 H_2O. C = 72·4; H = 7·1.
$C_{18}H_{21}O_3N$ requires C = 72·4; H = 7·0 per cent.

0·4712 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube $a_D - 7·88°$, whence $[a]_D - 209·0$.

It was shown that this base, which is not resolved by crystallisation, is a molecular mixture of *iso*codeine and *β-iso*codeine in the following way:

(1) *By Crystallisation of its Methiodide.*—Three grams of the base (m. p. 147—147·5°) were dissolved in ethyl alcohol (100 c.c.), excess of methyl iodide added, and the solution boiled for several minutes, when a quantity of glistening, prismatic crystals rapidly separated from the hot liquid. As the latter cooled, it was noticed that a further quantity of a substance different in appearance from that which at first separated was slowly being deposited. On again boiling the liquid, this second substance went into solution, leaving the first fraction undissolved. This beautifully crystalline methiodide was collected and after drying weighed 1·9 grams, which amounts to almost one-half the theoretical amount of salt possible from the 3 grams of base employed. On recrystallisation from water, it formed brilliant, anhydrous, prismatic needles which melted at 270° with slight decomposition:

0·4948 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube $a_D - 4·09°$, whence $[a]^t_D - 103·3°$.

This methiodide was identical in all respects with *iso*codeine methiodide, and on boiling its aqueous solution with sodium hydroxide, readily afforded methyl *iso*morphimethine, which melted at 168—169° (compare Schryver and Lees, Trans., 1901, 79, 563).

The alcoholic mother-liquor from the above *iso*codeine methiodide on cooling deposited a further crystalline salt in small, glistening, tabular prisms, and this was found to amount to 1·75 grams. On recrystallisation from water, in which it is a trifle more soluble than *iso*codeine methiodide, it formed small, glistening, tabular crystals, which melted at 215—216° without decomposition. It was anhydrous:

0·5010 dissolved in water and made up to 25 c.c. gave in a 2-dcm. tube $\alpha_D - 5·62°$, whence $[\alpha]_D - 140·2°$.

Further crystallisation from water caused no change in the properties of this methiodide, and on intimately mixing with *β-iso*codeine methiodide (p. 1415) the mixture melted at 215—216°. This second methiodide was, therefore, definitely identified as *β-iso*codeine methiodide.

(2) *By its Formation by Crystallising together equal amounts of* iso*Codeine and β-*iso*Codeine.*—*iso*Codeine (m. p. 171—172°) (0·343 gram) was dissolved together with an equal weight of *β-iso*codeine (syrupy base) in a small amount of warm ethyl acetate. On standing, slender prismatic needles were obtained identical in appearance with the base (m. p. 147—147·5°) from bromocodeide. 0·5 Gram of crystals was thus obtained. The melting point was also found to be identical, 147—147·5°, and was, moreover, not changed by further crystallisation or by mixing with the base from bromocodeide:

0·0936 gave 0·2495 CO_2 and 0·0592 H_2O. C = 72·7; H = 7·0.

$C_{18}H_{21}O_3N$ requires C = 72·4; H = 7·0 per cent.

0·2673 dissolved in chloroform and made up to 25 c.c. gave in a 2-dcm. tube $\alpha_D - 4·48°$, whence $[\alpha]_D - 209·5°$.

Complete identity was thus established between the base (m. p. 147—147·5°; $[\alpha]_D - 209·0°$) obtained from bromocodeide and the base formed by crystallising together equal amounts of *iso*codeine and *β-iso*codeine.

ADDENDUM.

While this paper was in the Press, a further communication by Knorr and Hörlein has appeared (*Ber.*, 1907, 40, 3342) in which these authors announce that, since their previous publication (*Ber.*, 1907, 40, 2032), their attention has been drawn to an abstract (*Chem. Zentr.*, 1907, i, 352) of the communication of Lees and Tutin "according to which the *iso*codeine of Schryver and Lees is a mixture of a base-*A* (m. p. 145°) and a base-*B* (m. p. 170°)." The actual abstract in the

Centralblatt gives the following characters for these two bases: ***A*-base**, m. p. 145—145·5°; $[\alpha]_D$ − 205° in chloroform; ***B*-base**, m. p. 171—172°; $[\alpha]_D$ − 155° in chloroform.

Knorr and Hörlein then state that "Hr. Stud. Grimme has confirmed the results of Lees and Tutin and has proved that the higher melting constituent (*B*-base of Lees and Tutin) is identical with *pseudo*codeine." This identification is stated to have been carried out "by comparison of the bases (m. p. 180—181°), their hydriodides, (m. p. 260—265°; $[\alpha]_D^{15}$ − 57°), methiodides (m. p. 270°), and the methine bases prepared from the latter (hydrochloride, m. p. about 150°; $[\alpha]_D$ − 154°)."

The statement that the *B*-base of Lees and Tutin is identical with neo*iso*codeine (*pseudo*codeine) is obviously incorrect, for the latter base has been shown by Knorr and Hörlein to have m. p. 180—181° and $[\alpha]_D$ − 94°, and these figures are confirmed by the author in the present paper. The statement of Knorr and Hörlein was, moreover, made with the following before them, in the same abstract in the *Centralblatt*: "Da die *B*-Base leicht aus Isomorphin durch methylierung mit Natrium und Dimethyl sulfat entsteht muss sie *Isokodein*, das kodein Analogen des Isomorphins, sein." The identity of the *B*-base (from bromocodeide) and the base produced by the methylation of *iso*morphine (from bromomorphide) was established by Lees and Tutin by the fact that both bases had the same melting point (171—172°) which was not changed when the specimens were mixed, by identity of specific rotatory power, and, furthermore, by the production from each specimen of methyl *iso*morphimethine (m. p. 168—169°; $[\alpha]_D$ + 64·6°).

Knorr and Hörlein have themselves shown that neo*iso*codeine (*pseudo*codeine) does not yield methyl *iso*morphimethine.

If further evidence were required to prove that the *B*-base of Lees and Tutin is not identical with neo*iso*codeine (*pseudo*codeine), it is afforded by the fact that an intimate mixture of the two bases was found to melt at 140—145°.

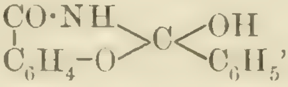
It may be that Hr. Stud. Grimme has isolated neo*iso*codeine (*pseudo*codeine) from among the products of the hydrolysis of bromocodeide, which is not altogether improbable, but it is difficult to understand how Knorr and Hörlein came to the conclusion that it was identical with a base of entirely distinct characters which they had not in hand for comparison.

THE WELLCOME CHEMICAL WORKS,
DARTFORD,
KENT.

CXXXVI.—*Phenylbenzometoxazone and Related Derivatives.*

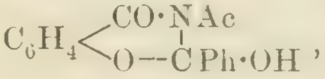
By Arthur Walsh Titherley.

In a previous paper (McConnan and Titherley, Trans., 1906, **89**, 1318), it has been shown that the most satisfactory explanation of the labile changes which occur between *O*- and *N*-acylsalicylamides is one involving the assumption of cyclic tautomerism. On this view, *N*-benzoylsalicylamide, $C_6H_4{<}\begin{smallmatrix}CO\cdot NH\cdot CO\cdot C_6H_5\\ OH\end{smallmatrix}$, in its pseudo-form was given the hydroxymetoxazone formula



$$\begin{matrix}CO\cdot NH\\ |\\ C_6H_4{-}O\end{matrix}{>}C{<}\begin{matrix}OH\\ C_6H_5\end{matrix},$$

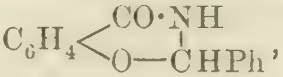
which would account for some of the anomalous properties of the substance and particularly for the ease with which *N*-benzoylbenzoylsalicylamide changes into the *O*-benzoyl isomeride, $C_6H_4{<}\begin{smallmatrix}CO\cdot NH_2\\ O\cdot CO\cdot C_6H_5\end{smallmatrix}$, as well as for the reverse change. Numerous examples of such metoxazone tautomerism were shown to exist among other acyl derivatives, but, although the reversible changes from *O*- to *N*-acyl forms were usually well defined, the hypothetical intermediate ring forms were generally too unstable to exist. One such cyclic derivative, however, *N*-acetyl-2 : 2-phenylhydroxybenzometoxazone,



$$C_6H_4{<}\begin{matrix}CO\cdot NAc\\ \quad\quad |\\ O{-}{-}CPh\cdot OH\end{matrix},$$

was described, but it was not found possible to confirm the structure of this compound. Another supposed cyclic derivative of similar metoxazone structure has since been shown by McConnan (Trans., 1907, **91**, 197) to possess another constitution.

It appeared desirable therefore to further test the validity of the ring hypothesis, and attempts were accordingly made by the author to prepare some stable metoxazone ring, with the result that the simple parent substance was obtained, namely, phenylbenzometoxazone,



$$C_6H_4{<}\begin{matrix}CO\cdot NH\\ \quad |\\ O{-}CHPh\end{matrix},$$

of which the hypothetical form of *N*-benzoylsalicylamide is the hydroxy-derivative. The synthesis of this parent ring was effected by the condensation* of salicylamide and benzaldehyde in presence of anhydrous sodium acetate at 140° according to Cebrian's method (*Ber.*, 1898, **31**, 1592), or in presence of a little alcoholic hydrochloric acid at 50°; and the results of this condensation have served to throw further valuable light on the problem of the acylsalicylamides. The two methods do not yield identical results; whilst the hydrochloric acid method yields only the metoxazone in fairly good yield, the sodium acetate condensation yields the metoxazone and an isomeric substance in proportions which vary according to the conditions of the experiment. This isomeride differs markedly from the metoxazone, which is insoluble in alkali and gives no ferric chloride reaction, by being readily soluble in sodium hydroxide, and by giving in alcoholic solution an intense violet colour with ferric chloride. From these features, it is evident that this compound is the open-chain derivative, benzylidenesalicylamide,

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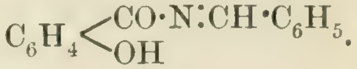
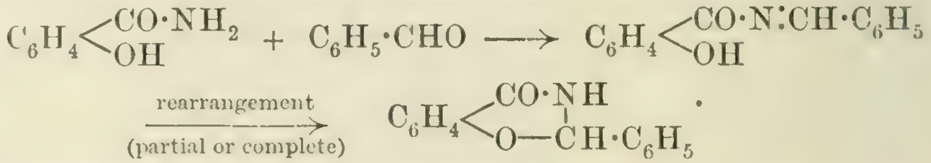
* Since carrying out this work, Keane and Nicholls have recently (Trans., 1907, **91**, 266) published an account of the same condensation by which they have isolated phenylbenzometoxazone. Their description of this substance entirely agrees with that of the author.



$$C_6H_4<\begin{matrix}CO\cdot N{:}CH\cdot C_6H_5\\ OH\end{matrix}.$$

It appeared likely that these two compounds (the open-chain and ring) stood in the same relation to each other that *N*-benzoylsalicylamide and its pseudo-ring form do, and it was therefore supposed that benzylidenesalicylamide would be labile and readily pass into the ring form, phenylbenzometoxazone, so that the mechanism of the salicylamide-benzaldehyde condensation could be expressed:

I.

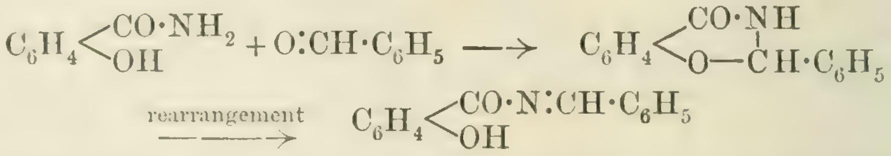


$$C_6H_4<\begin{matrix}CO\cdot NH_2\\ OH\end{matrix} + C_6H_5\cdot CHO \longrightarrow C_6H_4<\begin{matrix}CO\cdot N{:}CH\cdot C_6H_5\\ OH\end{matrix}$$

$$\xrightarrow[\text{(partial or complete)}]{\text{rearrangement}} C_6H_4<\begin{matrix}CO\cdot NH\quad\\ \quad\;\; |\\ O-CH\cdot C_6H_5\end{matrix}.$$

An alternative mechanism, however, is possible, involving the production of the metoxazone first and its subsequent rearrangement thus:

II.



$$C_6H_4<\begin{matrix}CO\cdot NH_2\\ OH\end{matrix} + O{:}CH\cdot C_6H_5 \longrightarrow C_6H_4<\begin{matrix}CO\cdot NH\quad\\ \quad\;\; |\\ O-CH\cdot C_6H_5\end{matrix}$$

$$\xrightarrow{\text{rearrangement}} C_6H_4<\begin{matrix}CO\cdot N{:}CH\cdot C_6H_5\\ OH\end{matrix}$$

Between these two alternatives it is easy to decide, and there can be no doubt that the latter (II) does not hold for the following reasons.

(1) *N*-Methylsalicylamide should condense with benzaldehyde according to (II), yielding phenyl-*N*-methylbenzometoxazone. When the condensation is attempted, however, no reaction whatever takes place.

(2) Phenylbenzometoxazone shows no tendency to rearrange to the benzylidenesalicylamide formed in the salicylamide-benzaldehyde synthesis. A number of experiments in which the metoxazone was heated with sodium acetate and benzaldehyde under the conditions of the synthesis gave negative results.

It is necessary therefore to assume that the first product of the interaction of benzaldehyde and salicylamide is (in accordance with mechanism I) benzylidenesalicylamide, and on this assumption it would follow that the final rearrangement to the ring is incomplete in presence of sodium acetate, but complete in presence of hydrochloric acid owing to its strong catalytic influence.

This view, however, required some modification inasmuch as it was found that free benzylidenesalicylamide was quite stable towards hydrochloric acid, as well as sodium acetate and benzaldehyde, and under no circumstances has it been found possible to transform it into its ring isomeride. On the other hand, the ring (phenylbenzometoxazone) may be transformed into an open-chain compound, benzylidenesalicylamide,

$C_6H_4{<}^{CO{\cdot}N{:}CH{\cdot}C_6H_5}_{OH}$, not identical with the above (synthetic) benzylidenesalicylamide.

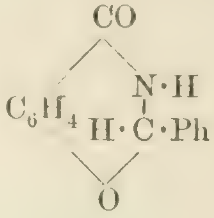
The rearrangement is quantitative and is effected by treatment with pyridine and potassium hydroxide. This important development makes it clear that there are two benzylidenesalicylamides, and, moreover, one of these (that obtained by rearrangement) readily passes over into its isomeride, phenylbenzometoxazone, on melting or on heating in presence of certain solvents. The relation between these two compounds, the labile open-chain and the more stable phenylbenzometoxazone, affords a striking confirmation of the metoxazone theory of cyclic tautomerism as applied to the acylsalicylamides; the main difference between the two parallel cases lying in the fact that in the former the ring is stable, whilst in the latter (acylsalicylamides) the ring is unstable.

The existence of two benzylidenesalicylamides is intelligible on the assumption that they are geometrical isomerides, similar to the stereoisomeric oximes, but the author is not aware of any other examples of geometrical isomerism among compounds containing the grouping

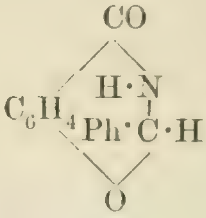
$$CO{\cdot}N{:}CHR.$$

Both benzylidene derivatives appear as amorphous substances having similar physical characters, and each gives a deep purple colour in acetone solution with alcoholic ferric chloride. There are, however, certain well-defined differences between the isomerides, for example, one retains its amorphous character and cannot be crystallised, whilst the other can be obtained crystalline; but the most important distinction lies in the stability of the one as compared with the rearrangement-capacity of the other. Having regard to the general principle that *cis-* or *syn*-geometrical isomerides only are derived by the rupture of cyclic compounds, the configuration of the unstable benzylidenesalicylamide obtained by rearrangement of phenylbenzometoxazone follows. It has been called *syn*, whilst its stable isomeride obtained synthetically has been called *anti*. It is to be noted that the ring compound, phenylbenzometoxazone, may be expected to appear in stereoisomeric forms inasmuch as in the first place it contains an asymmetric carbon atom and in the second place the nitrogen atom might occasion geometrical isomerism in accordance with the Hantzsch-Werner theory. There should be thus two enantiomorphously related pairs having the *syn*-configuration and two having the *anti*-configuration. Thus assuming the phenyl group in the *syn*-form to lie close to the hydrogen atom attached to nitrogen, and away from it in the *anti*-form, phenylbenzometoxazone might be expected to appear in the four following configurations :

A.

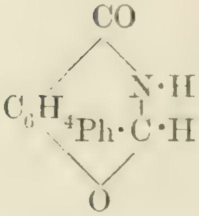


d-syn.

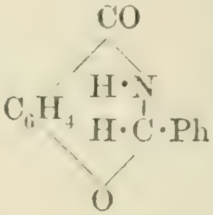


l-syn.

B.



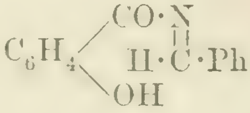
d-anti.



l-anti.

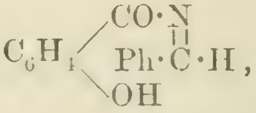
There is only one compound known (inactive), namely, that melting at 169°, which is doubtless racemic, but there is nothing to show which of the alternative configurations, *syn*- or *anti*-, this compound possesses, although it is fair to assume from the reasoning developed below that the known phenylbenzometoxazone is $(d + l)$ *syn*.

Writing the projection formulæ of the two possible benzylidenesalicylamides



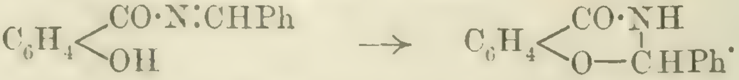
I.

and



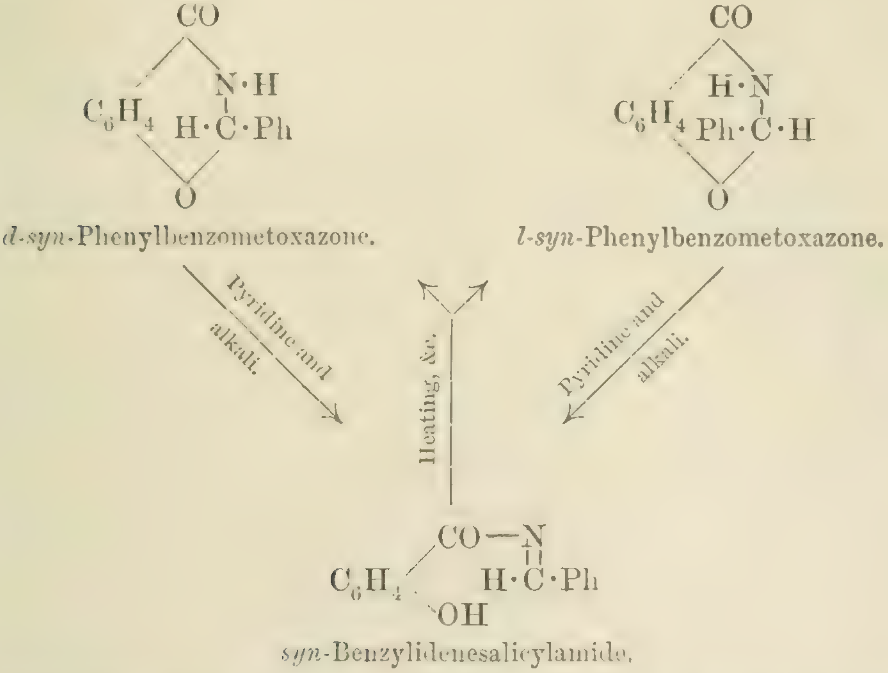
II.

it is evident that the easy transformation of the one into the metoxazone, whilst the other is perfectly stable, cannot be accounted for by any difference in propinquity of nitrogen favouring the wandering of the hydroxylic hydrogen atom in the change :



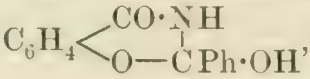
$$C_6H_4\left<\begin{matrix}CO\cdot N\!:\!CHPh\\OH\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}CO\cdot NH\\O-CHPh\end{matrix}\right..$$

Examination of the model formulæ makes this point more clear than can be elucidated by plane formulæ, and the only satisfactory way of explaining the difference in stability between the two isomerides is to assume some "steric hindrance" to be exercised by the large phenyl group preventing rearrangement in configuration (II) above, which is therefore assigned to the stable *anti*-isomeride, whilst *syn*-benzylidenesalicylamide is given configuration (I). On this assumption, phenylbenzometoxazone (m. p. 169°) must have the $(d+l)$ *syn*-configuration *A*, as it is clear on consulting the model formulæ that when *syn*-benzylidenesalicylamide (I) rearranges it must give the enantiomorphously related forms of the above racemic compound *A*, each component of which on rearrangement (by pyridine and alkali) must conversely give *syn*-benzylidenesalicylamide. These relations are brought out in the scheme:



On similar lines, *anti*-benzylidenesalicylamide, if it could be induced to rearrange simply to a ring, should yield the unknown $(d+l)$ *anti* phenylbenzometoxazone. All attempts to effect this change have failed.

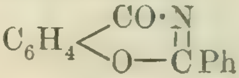
With regard to the mechanism of the condensation between benzaldehyde and salicylamide, in which it has been shown that benzylidenesalicylamide is the first product of the reaction, it must follow from what has been stated that the *syn*-isomeride only is produced when alcoholic hydrochloric acid is employed as condensing agent, the *syn*-isomeride then rearranging completely to phenylbenzometoxazone. On the other hand, when sodium acetate is employed (at higher temperatures) as the condensing agent, it is evident that both *syn*- and *anti*-benzylidenesalicylamides are first produced, but not in equimolecular proportions. The *syn*-isomeride then completely rearranges to phenylbenzometoxazone, so that a mixture of this compound and *anti*-benzylidenesalicylamide results. No reason has been discovered which would account for the variations in the relative amounts produced by varying the conditions of the condensation.

In the acylsalicylamide group, as was pointed out (*loc. cit.*), the ring forms are usually unstable and intermediate in the change from *O*-acyl to *N*-acyl derivatives and *vice versâ*. All attempts to isolate the compound,  $C_6H_4{<}\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}Ph\cdot OH\end{array}$, lying as the pseudo-form between *O*-benzoyl- and *N*-benzoyl-salicylamide have failed, and it would appear therefore that the presence of the hydroxyl group renders such metoxazone rings unable to exist or at least very unstable.

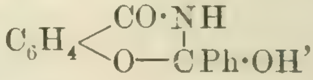
As, however, the theory of cyclic tautomerism of the acylsalicylamides (McConnan and Titherley, *loc. cit.*) involves the fundamental assumption that such hydroxy-metoxazones play an essential part in the labile changes, it was of importance to establish a direct relation between *N*-benzoylsalicylamide and phenylbenzometoxazone, or find further evidence of the alternative cyclic formula of the former. To this end, attempts were made with *N*-benzoylsalicylamide:

(1) To reduce it to phenylbenzometoxazone.

(2) To methylate it and obtain methoxyphenylbenzometoxazone.

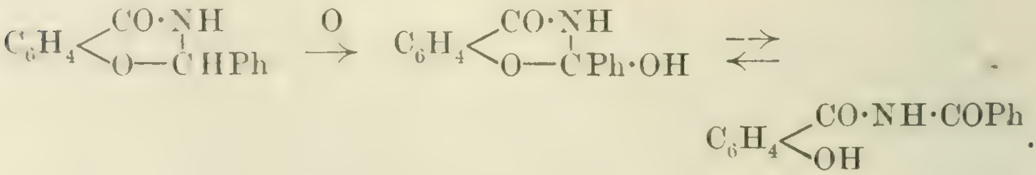
(3) To dehydrate it and isolate the ring derivative,  $C_6H_4{<}\begin{array}{l}CO\cdot N\\ O-\overset{\|}{C}Ph\end{array}$.

Also experiments with phenylbenzometoxazone:

(4) To oxidise and convert it into  $C_6H_4{<}\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}Ph\cdot OH\end{array}$, which should be identical with *N*-benzoylsalicylamide.

Experiments (1), (2), and (3), although carried out in a variety of ways, produced entirely negative results, which make it evident that the stable form of *N*-benzoylsalicylamide possesses the open-chain and not the ring structure.

The oxidation (4) of phenylbenzometoxazone, however, gave definite results. Whilst the majority of oxidising agents, such as bromine water, potassium permanganate, &c., decomposed the molecule giving a variety of products, oxidation of the metoxazone in cold concentrated sulphuric acid (in which it is soluble without change) by means of a glacial acetic solution of chromic acid produced an excellent yield of *N*-benzoylsalicylamide, thus:



$$C_6H_4{<}\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}HPh\end{array} \xrightarrow{O} C_6H_4{<}\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}Ph\cdot OH\end{array} \rightleftarrows C_6H_4{<}\begin{array}{l}CO\cdot NH\cdot COPh\\ OH\end{array}.$$

This unmistakable relation between phenylbenzometoxazone and *N*-benzoylsalicylamide, taken into account with the labile relations between *syn*-benzylidenesalicylamide and phenylbenzometoxazone, furnishes abundant confirmation of the theory of cyclic tautomerism put forward in connexion with the acylsalicylamide group.

EXPERIMENTAL.

Preparation of Phenylbenzometoxazone.

The condensation of benzaldehyde and salicylamide was effected by means of (1) anhydrous sodium acetate; (2) alcoholic hydrochloric acid. In (1), a mixture of phenylbenzometoxazone and *anti*-benzylidenesalicylamide was formed in proportions which varied with the conditions of the experiment; in (2), phenylbenzometoxazone only was produced, but in neither case was the condensation complete.

(1) 13·7 Grams of salicylamide, 15·6 grams of benzaldehyde, and 8·5 grams of powdered anhydrous sodium acetate were heated at 140° for forty-five minutes. The mixture, which was stirred occasionally, frothed gently and water was disengaged. When cold, the mass was treated with about 100 c.c. of water, disintegrated, and digested with an excess of 10 per cent. sodium hydroxide in order to remove *anti*-benzylidenesalicylamide and unchanged salicylamide. The insoluble solid (phenylbenzometoxazone) was washed with 50 per cent. aqueous alcohol to remove the benzaldehyde adhering to it and the remaining white powder was recrystallised from hot alcohol, from which it separated in fine needles. From the alcoholic mother liquor, a second crop was obtained by adding a little sodium hydroxide to clear the turbid solution and diluting with water. The total yield of pure metoxazone only amounted to 6·5 grams. It melted at 166—167°, but after further recrystallisation at 169°, and then gave no coloration in alcoholic solution with ferric chloride:

0·1614 gave 9·0 c.c. nitrogen at 23° and 762 mm. N = 6·30.

$C_{14}H_{11}O_2N$ requires N = 6·22 per cent.

Modification in this method of preparation led to no increase, but frequently to a decrease, in the yield.

(2) A mixture of 15·5 grams of salicylamide and 12·2 grams of benzaldehyde was warmed to 50° and treated with 1 c.c. of a saturated solution of hydrogen chloride in alcohol. The mixture, which was clear at first, rapidly became turbid, owing to the separation of water, and in a few minutes a thick white mass of fine needles separated. The whole was kept at 60° for twenty minutes and the resulting cake, after cooling, was triturated and washed with 90 per cent. aqueous alcohol. The insoluble residue, consisting of a mixture of the

metoxazone and salicylamide, was digested in the cold with aqueous sodium hydroxide, washed, and recrystallised from alcohol. The pure phenylbenzometoxazone thus obtained melted sharply at 169°, and a less pure crop was isolated by working up the alcoholic washings. The total yield was 13·5 grams, and there was no appreciable quantity of *anti*-benzylidenesalicylamide formed. It is evident that for the preparation of the metoxazone this condensation (2) is to be preferred to (1):

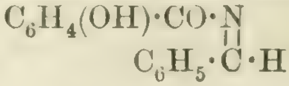
0·2054 gave 0·5608 CO_2 and 0·0942 H_2O. C = 74·46 ; H = 5·09.
0·2150 ,, 11·4 c.c. nitrogen at 19° and 753 mm. N = 6·06.[*]
$C_{14}H_{11}O_2N$ requires C = 74·66 ; H = 4·89 ; N = 6·22 per cent.

Molecular weight determination by the freezing point method :
0·1970 in 20·340 acetic acid gave Δt 0·190°. M.W. = 199.
0·4304 ,, ,, ,, ,, Δt 0·396°. M.W. = 211.
$C_{14}H_{11}O_2N$ requires M.W. 225.

The properties of phenylbenzometoxazone observed by the author agree closely with those described by Keane and Nicholls (*loc. cit.*).

Oxidation of Phenylbenzometoxazone.—Two grams of phenylbenzometoxazone were dissolved in 30 grams of concentrated sulphuric acid, and the resulting yellow solution was treated gradually with continual stirring with a solution of 3·5 grams of chromic anhydride in 30 grams of glacial acetic acid. The temperature was not allowed to exceed 30°. After half an hour, the resulting greenish-yellow syrup was poured into ice-cold water. A discoloured, white precipitate was produced which, after washing, was purified by crystallisation from 90 per cent. alcohol, using animal charcoal. The substance separated in very small needles melting at 208°, which were easily identified as *N*-benzoylsalicylamide owing to the characteristic properties of this substance.

Attempted Synthesis of Phenyl-N-*methylbenzometoxazone.*—Fifteen grams of *N*-methylsalicylamide, 12 grams of anhydrous sodium acetate, and 10·6 grams of benzaldehyde were heated for forty-five minutes at 140—150°. The mixture was cooled, treated with water, and the benzaldehyde removed by steam. The residual oil, on cooling, set to a crystalline mass. It weighed 14 grams and consisted of unchanged *N*-methylsalicylamide, and since 10 grams of benzaldehyde were recovered it was clear that no condensation had taken place.

anti-*Benzylidenesalicylamide*, 
$\begin{array}{l}C_6H_4(OH)\cdot CO\cdot N\\ \qquad\qquad\ \ C_6H_5\cdot C\cdot H\end{array}$.—This compound,

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[*] The nitrogen values for the group of compounds described in this paper were liable to be low, owing to the difficulty of completing the combustion. In most cases, it was necessary to continue the combustion about an hour longer than is usually the case by the copper oxide method.

which is produced in the sodium acetate condensation of benzaldehyde and salicylamide, was best obtained as follows:

An intimate mixture of 13·7 grams of salicylamide, 12 grams of benzaldehyde, and 12 grams of anhydrous sodium acetate were heated at 140—150° for an hour and three quarters with occasional stirring. On cooling, the thick, viscous mass became almost solid. It was treated with warm water to remove the sodium acetate, and the insoluble, semi-solid residue was dissolved in about 100 c.c. of warm chloroform. The filtered chloroform solution containing the *anti*-benzylidenesalicylamide together with unchanged salicylamide and benzaldehyde was then shaken with 10 per cent. aqueous sodium hydroxide; the alkaline extract was filtered, diluted to 1500 c.c., and acidified with hydrochloric acid. In this way, *anti*-benzylidenesalicylamide was obtained as a voluminous, amorphous, white precipitate, whilst the salicylamide remained in solution. The precipitate was washed and dried on porous earthenware. It weighed 16·5 grams, but was not pure and melted indefinitely between 110° and 160°. Owing to its persistent amorphous character it was difficult to purify, and crystallisation was impossible. By repeatedly dissolving it in chloroform and partly precipitating with light petroleum (b. p. 30—70°), it was finally obtained pure. The purification was checked by analysis as the pure product has an indefinite melting point (170—190°). As the purification proceeded, a very pronounced decrease in solubility in alcohol and ether was noticed, so that, whilst the approximately pure substance is fairly easily soluble, pure *anti*-benzylidenesalicylamide is sparingly soluble.

The chloroform solution, remaining after the above extraction with sodium hydroxide, contained benzaldehyde and 2·5 grams of phenylbenzometoxazone which was isolated. The following figures were obtained with the pure *anti*-benzylidenesalicylamide:

0·2466 gave 0·6752 CO_2 and 0·1158 H_2O. C = 74·63; H = 5·21.
0·1064 ,, 5·7 c.c. nitrogen at 19° and 769 mm. N = 6·23.
$C_{14}H_{11}O_2N$ requires C = 74·66; H = 4·89; N = 6·22 per cent.

Molecular weight by (1) freezing point method:

0·1891 in 21·250 acetic acid gave Δ 0·15°. M.W. = 229.

(2) Boiling point method:

0·1963 in 21·515 chloroform gave Δ 0·135°. M.W. = 243.
$C_{14}H_{11}O_2N$ requires M.W. = 225.

anti-*Benzylidenesalicylamide* is an amorphous, white powder showing marked electrification on contact. It is insoluble in water or light petroleum and sparingly soluble in cold alcohol, ether, chloroform, or acetic acid and in hot benzene. It is not changed on heating with acetic acid and anhydrous sodium acetate or benzaldehyde, or a mixture of this and sodium acetate at 140°, and is unaffected by hydrogen chloride at this temperature. It is also indifferent towards pyridine or alcoholic hydrogen chloride, is unchanged on melting, and shows no tendency whatever to undergo rearrangement to phenylbenzometoxazone (compare its *syn*-isomeride).

Its alcoholic or acetone solution gives a deep purple colour with ferric chloride. It is readily soluble in aqueous sodium hydroxide, and the resulting sodium derivative is quite stable in aqueous solution in the cold, although on boiling with an excess of alkali it is decomposed yielding benzaldehyde and salicylamide. When titrated with $N/10$-sodium hydroxide in alcoholic solution, using phenolphthalein as indicator, an indefinite end reaction is obtained, but by adding an excess of sodium hydroxide and titrating back with $N/10$ hydrochloric acid until a permanent turbidity is produced, a fairly definite result can be obtained:

0·3142 required 12·0 c.c. $N/10$ NaOH = 0·048 gram NaOH.
$C_{14}H_{11}O_2N$ requires 0·055 gram NaOH.

The aqueous solution of the sodium salt at once reduces potassium permanganate; on standing, the sodium salt is decomposed by atmospheric CO_2 and free *anti*-benzylidenesalicylamide is obtained as an amorphous precipitate.

anti-*Benzylidenesalicylamide benzoate*, $BzO{\cdot}C_6H_4{\cdot}CO{\cdot}N{:}CH{\cdot}C_6H_5$, is readily formed by the Schotten-Baumann benzoylation of the *anti*-derivative dissolved in an excess of dilute aqueous sodium hydroxide. The benzoyl derivative separated as an amorphous, granular powder, which was purified by washing carefully with alcohol and subsequent precipitation from glacial acetic solution with water. It was finally purified by dissolving it in a mixture of benzene and alcohol and precipitating by light petroleum. The purified substance, which retained its amorphous character, could not be crystallised and melted indefinitely at 180—200°. It gave no coloration with ferric chloride:

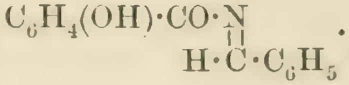
By Kjeldahl's method, 0·2062 gave 0·01156 NH_3. N = 4·61.
$C_{21}H_{15}O_3N$ requires N = 4·26 per cent.

The same benzoyl derivative was also prepared by treating 1 gram of *anti*-benzylidenesalicylamide dissolved in 5 grams of pyridine with 1 gram of benzoic anhydride. The mixture was kept at 50° for thirty minutes, cooled, treated with about 70 c.c. of alcohol until the benzoyl derivative showed signs of separating, and, finally, about 70 c.c. of water were gradually added. The benzoyl derivative (1 gram) separated as a white, amorphous, granular precipitate, melting at 170—200°, and purer than that obtained by the Schotten-Baumann method. By dissolving in pyridine and precipitating with alcohol, the nearly pure substance was obtained melting between 202° and 220°:

0·1182 gave 4·9 c.c. nitrogen at 20° and 740 mm. N = 4·60.
$C_{21}H_{15}O_3N$ requires N = 4·26 per cent.

anti-*Benzylidenesalicylamide benzoate* is an amorphous powder, insoluble in water or alcohol, very sparingly soluble in ether, moderately so in cold benzene, and readily so in hot benzene, glacial acetic acid, acetone, or chloroform.

syn-*Benzylidenesalicylamide*,



$$\begin{array}{r} C_6H_4(OH)\cdot CO\cdot N \\ \| \;\; \\ H\cdot C\cdot C_6H_5 \end{array}.$$

This compound is produced as its sodium derivative by the rearrangement of phenylbenzometoxazone by pyridine and alkali. A slightly impure amorphous and a pure crystalline variety have been isolated.

A solution of 5 grams of phenylbenzometoxazone in 35 grams of pyridine was shaken vigorously with 7—8 c.c. of 50 per cent. aqueous potassium hydroxide in the cold for an hour, at the end of which time the bright yellow colour* which was first produced mostly disappeared. The mixture in two immiscible layers was treated with water to form a clear solution which was then diluted to 1600 c.c. This was treated gradually, in the cold, with dilute hydrochloric acid in quantity more than sufficient to neutralise the alkali and pyridine. *syn*-Benzylidenesalicylamide separated in a practically pure form as a white, amorphous, granular precipitate with no tendency to become oily if the mixture was kept well cooled; if an excess of hydrochloric acid is not used, the precipitate carries down some pyridine with it.. After washing repeatedly with cold water and drying in a vacuum on porous earthenware, it was obtained as a light, white, amorphous solid, showing electrical properties like its isomeride, and weighing 5 grams, the yield being quantitative:

0·1736 gave 9·4 c.c. nitrogen at 21° and 757 mm. N = 6·14.
$C_{14}H_{11}O_2N$ requires N = 6·22 per cent.

Molecular weight determination by the boiling point method:

0·1702 in 21·670 chloroform gave Δ 0·115°. M.W. = 246.
0·3004 ,, ,, ,, Δ 0·235°. M.W. = 212.
$C_{14}H_{11}O_2N$ requires M.W. = 225.

The *amorphous syn*-derivative melts indefinitely between 140° and 167° and undergoes rearrangement at the same time to phenylbenzometoxazone (m. p. 167°), which solidifies as a crystalline mass on cooling. The change is almost quantitative. Amorphous syn-*benzylidenesalicylamide* is insoluble in water or alcohol, and is almost insoluble in ether or cold glacial acetic acid. It is sparingly soluble in boiling alcohol, which slowly changes it to a crystalline form, but prolonged boiling with alcohol also partially transforms it into phenylbenzometoxazone. It is also sparingly soluble in chloroform or benzene and moderately so in warm acetone. A hot acetone or benzene solution on cooling deposits the substance in the amorphous form. Amorphous *syn*-benzylidenesalicylamide is difficultly soluble in cold dilute aqueous sodium hydroxide, owing to the formation of a sparingly soluble sodium salt, which dissolves on warming and separates out again on cooling. The amorphous *syn*-derivative dissolves at once in sodium hydroxide in presence of alcohol, and the resulting solution of the sodium salt gives a precipitate of the amorphous *syn*-compound on treatment with acids or on exposure to atmospheric carbon dioxide. The amorphous compound on heating with 20 per cent. sodium hydroxide becomes oily and subsequently dissolves; the solution on cooling deposits an amorphous sodium salt, but on long heating it is decomposed, giving benzaldehyde and salicylamide like the *anti*-isomeride. The phenolic properties of the *syn*-derivative are evident from its behaviour with sodium hydroxide and with ferric chloride. In warm acetone solution, it gives a deep purple colour with alcoholic ferric chloride, and in warm alcoholic solution it gives a reddish-yellow colour which is discharged by an excess of alcohol.

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* This yellow colour is probably due to the linking oxygen atom becoming quadrivalent and yielding an alkali derivative as in the pyrone group.

Crystalline syn-benzylidenesalicylamide is produced in a very pure form, melting at 182°, by boiling the amorphous variety with glacial acetic acid for a short time. The amorphous substance readily dissolves in the boiling acid, but, if cooled immediately, separates unchanged; on boiling for fifteen minutes and cooling, the pure crystalline *syn*-benzylidenesalicylamide, being almost insoluble, separates as a mass of bright, silky needles, but as there is simultaneously partial rearrangement to phenylbenzometoxazone which remains in solution, the transformation, which has only been studied qualitatively as yet, is accompanied by loss in weight.

A better yield of the crystalline *syn*-derivative is obtained when the amorphous form is boiled in a reflux apparatus with alcohol. In one experiment, 2 grams of the amorphous *syn*-compound were boiled with 80 c.c. of absolute alcohol for an hour. The solid did not dissolve more than partially at any time during the boiling, but it slowly changed to a mass of very fine, small, silky needles, melting at 180—182°, and weighing 1·2 grams. It was evident here as with the acetic acid transformation that some other change had occurred, inasmuch as practically 2 grams should have been obtained of such an insoluble compound. The alcoholic filtrate, on standing, deposited white, crystalline crusts, weighing 0·4 gram, of a compound [*] melting at 175°, which appears to be an alcohol-additive compound, and the mother liquor was found to contain 0·25 gram of the amorphous *syn*-derivative together with a small quantity (0·08 gram) of phenylbenzometoxazone, showing that slight rearrangement had occurred.

Crystalline *syn*-benzylidenesalicylamide gave the following figures :

0·1613 gave 0·4384 CO_2 and 0·0729 H_2O. C = 74·14 ; H = 5·02.
0·1436 ,, 7·8 c.c. nitrogen at 20° and 764 mm. N = 6·24.
$C_{14}H_{11}O_2N$ requires C = 74·66 ; H = 4·89 ; N = 6·22 per cent.

Molecular weight by boiling point method :

0·2292 in 22·110 chloroform gave Δ 0·17°. M.W. = 220.
$C_{14}H_{11}O_2N$ requires M.W. = 225.

Crystalline syn-*benzylidenesalicylamide* differs distinctly, although slightly in properties, from the amorphous variety. It is rather less soluble in solvents and is characterised by its very sparing solubility in alcohol or acetic acid. It is scarcely affected by dilute sodium hydroxide, although readily soluble in presence of a little alcohol ; the alkaline solution on acidification gives a white precipitate of the amorphous variety. The crystalline substance in warm acetone solution gives a purple colour with alcoholic ferric chloride, and it is evident from these reactions that the transformation from the amorphous to the crystalline form does not affect the chemical character of the substance. On melting (at 182°), the crystalline compound is transformed quantitatively into the isomeric phenylbenzometoxazone melting at 168°. The chief difference between the two varieties of *syn*-benzylidenesalicylamide lies in their behaviour on benzoylation. Both give anomalous results (see below), owing probably to partial rearrangement to the metoxazone taking place.

Benzoylation of syn-*Benzylidenesalicylamide.*

Attempts were made to prepare the benzoyl derivative from the amorphous form by (*a*) the Schotten-Baumann method, (*b*) by means of pyridine and benzoic anhydride, and (*c*) by pyridine and benzoyl chloride.

Method (*a*) gave long, silky needles melting at 185—187°, but the reaction proceeds with difficulty and the yield is small. An oily mixture first results, which becomes crystalline on standing. After

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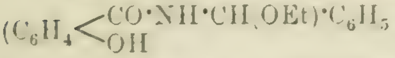
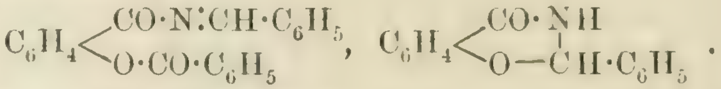
[*] This compound is at present under investigation ; it gave, on analysis, N = 5·47.  $(C_6H_4<^{CO\cdot NH\cdot CH(OEt)\cdot C_6H_5}_{OH}$ requires N = 5·16 per cent.) ; it crystallises from alcohol in plates, is soluble in sodium hydroxide, and gives a violet ferric chloride reaction.

purification by digestion with sodium hydroxide and twice recrystallising from alcohol, a benzoyl derivative (m. p. 185°) was obtained, which was sparingly soluble in cold alcohol and gave no ferric chloride reaction. Analysis showed that the substance was probably a double compound of phenylbenzometoxazone and (presumably) *O*-benzoyl-*syn*-benzylidenesalicylamide,



$$C_6H_4<^{CO\cdot N:CH\cdot C_6H_5}_{O\cdot CO\cdot C_6H_5}, \quad C_6H_4<^{CO\cdot NH}_{O-\overset{|}{C}H\cdot C_6H_5}.$$

0·2363 gave 9·9 c.c. nitrogen at 23° and 756 mm. N = 4·70.
0·1376 ,, 5·8 ,, ,, ,, 18° and 769 mm. N = 4·92.

By Kjeldahl's method :

0·2938 gave 0·1717 NH_3. N = 4·81.

$C_{35}H_{26}O_5N_2$ requires N = 5·05 per cent.

The compound is almost insoluble in cold alcohol, moderately soluble in acetic acid, and readily so in chloroform.

Method (*b*) was conducted as follows : 1 gram of the amorphous compound suspended and dissolved in 6 grams of pyridine was treated with 1 gram of benzoic anhydride. The gelatinous solid dissolved slowly and the whole was left for twelve hours. It was then treated with about 40 c.c. of pure ether and the ethereal mixture was shaken with dilute sulphuric acid to remove pyridine. On evaporation, the ethereal solution deposited white crusts, which were washed with cold alcohol. The solid consisted of a mixture of two benzoyl derivatives, which were separated by dissolving in about 120 parts of boiling alcohol. On cooling, the double compound melting at 185° separated in fine needles, which were purified by recrystallisation from alcohol. The pure substance (m. p. 187°) weighed 0·5 gram :

0·1869 gave 7·8 c.c. nitrogen at 14° and 756 mm. N = 4·88.

$C_{35}H_{26}O_5N_2$ requires N = 5·05 per cent.

The alcoholic mother liquor from this compound on standing deposited short, glistening prisms (0·4 gram), which after recrystallisation from alcohol (in which they were more soluble than the compound melting at 187°) melted at 167°. Analysis showed that this substance was also apparently a double compound of phenylbenzometoxazone and a benzoyl derivative :

0·1283 gave 0·3588 CO_2 and 0·0610 H_2O. C = 76·2 ; H = 5·2.
0·2528 ,, 12·0 c.c. nitrogen at 20° and 757 mm. N = 5·35.

$C_{35}H_{26}O_5N_2$ requires C = 75·81 ; H = 4·7 ; N = 5·05 per cent.

Method (*c*) gave similar results to (*b*). 1·5 Grams of the amorphous compound in 10 grams of pyridine were treated gradually at 0° with 1·5 grams of benzoyl chloride. The resulting solution, which became pink, was kept at 0° for thirty minutes, treated with ether, and worked up as in (*b*). A mixture of the same two double compounds (m. p. 185° and 165° respectively) was obtained which were separated by fractional crystallisation from alcohol.

The benzoylation of crystalline *syn*-benzylidenesalicylamide gave only the double compound melting at 167°, and a simple benzoyl derivative could not be isolated. By the wet method with alkali and benzoyl chloride, no action takes place, but with pyridine and benzoic anhydride or benzoyl chloride, benzoylation readily takes place, and on working up by the ether treatment (see p. 1432, *b*) the double compound melting at 167° can be readily isolated as small, glistening prisms:

0·3440 gave 15·2 c.c. nitrogen at 22° and 750 mm. N = 4·91.

$C_{35}H_{26}O_5N_2$ requires N = 5·05 per cent.

On dissolving in glacial acetic acid, the double compound evidently dissociates into its components, as shown by a molecular weight determination (freezing point method):

0·1890 in 21·18 acetic acid gave Δ 0·14. M.W. = 247.

0·4042 ,, ,, ,, ,, Δ 0·30. M.W. = 246.

$C_{14}H_{11}O_2N + C_{21}H_{15}O_3N$ requires mean M.W. = 277.

The existence of the above double compounds is difficult to account for, and the fact that on benzoylation the amorphous *syn*-derivative yields a mixture of compounds would appear to suggest that the former is itself a mixture. The benzoyl derivatives are being submitted to investigation and a further study of the benzoylation of this group of compounds will be made.

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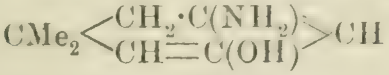
CXXXVII.—*iso*Nitroso- and Nitro-dimethyldihydroresorcin.

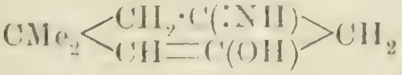
By PAUL HAAS.

SOME time ago (Trans., 1906, 89, 191) it was shown that when dimethyldihydroresorcin reacts with ammonia in aqueous solution, condensation takes place between the two substances with the formation of a monoamine of the formula $C_8H_{13}ON$. In order to determine whether this substance was a primary (I) or a secondary (II) amine,



$$CMe_2<\begin{matrix}CH_2\cdot C(NH_2):\\CH{=}C(OH)\end{matrix}>CH$$

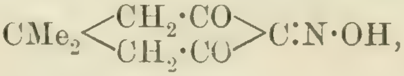
(I.)



$$CMe_2<\begin{matrix}CH_2\cdot C(:NH)\\CH{=}C(OH)\end{matrix}>CH_2$$

(II.)

it was decided to study its behaviour towards nitrous acid. A substance of the formula (I) would be expected to regenerate dimethyldihydroresorcin on treatment with nitrous acid, whereas a substance of formula (II) should give a nitrosoamine. When, however, a solution of the base mixed with potassium nitrite is acidified with hydrochloric acid, a violet compound is obtained, which has the composition $C_8H_{12}O_2N_2$ required by a nitrosoamine, but has none of the properties of such a compound. In view of the fact that the nitrous acid appeared not to have reacted with the nitrogen atom at all, it was thought advisable to investigate the action of nitrous acid on dimethyldihydroresorcin itself, and it was found that a substance of the composition $C_8H_{11}O_3N$ was produced. This formula might be taken to represent a nitroso-derivative of dimethyldihydroresorcin, but the fact that the substance does not give the Liebermann reaction shows that it does not contain the ordinary nitroso-grouping, and, inasmuch as it is able to yield a dioxime, it must be regarded as an *iso*nitroso-derivative of dimethyldihydroresorcin of the formula



$$CMe_2{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}{>}C{:}N\cdot OH,$$

(III.)

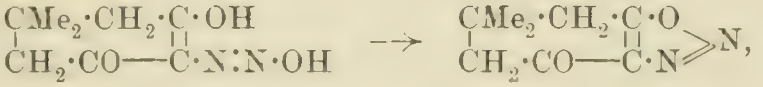
and is therefore a cyclic α-oximino-ketone. According to Guinchard (*Ber.*, 1899, **32**, 1723) and Whiteley (Trans., 1903, **83**, 24), such compounds give coloured alkali and ferrous salts, both of which characteristics are exhibited in marked degree by this substance, the potassium and ammonium salts being peacock-blue and violet respectively, while the ferrous salt is a deep azure-blue.

Attempts to convert iso*nitrosodimethyldihydroresorcin* into the corresponding nitro-compound by oxidising it with hydrogen peroxide resulted in a fission of the ring with the formation of ββ-dimethylglutaric acid, carbon dioxide, and oxides of nitrogen, which proved that the nitrogen must have been attached to the carbon atom in the para-position relative to the *gem*-dimethyl grouping. The conversion of the *iso*nitroso-compound into the nitro-compound may, however, be readily effected by saturating an ethereal solution of the former compound with oxides of nitrogen. Subsequently it was found that *nitrodimethyldihydroresorcin* could be more easily prepared by bubbling oxides of nitrogen into an ethereal suspension of dimethyldihydroresorcin itself. The nitro-compound is practically colourless, but it yields a pale yellow potassium salt and a bright yellow ammonium salt; in alcoholic solution, it gives with ferric chloride a yellowish-red colour, and with ferrous sulphate a reddish-brown.

Both *iso*nitroso- and nitro-dimethyldihydroresorcin yield on reduction the same amine, $C_8H_{13}O_2N$, but as the *iso*nitroso-compound is very sensitive to heat and decomposes readily, the reduction is more easily effected by starting from the nitro-compound. The free amine itself was not isolated, but it was characterised in the form of its hydrochloride, its platinum salt, and its acetyl derivative. When the hydrochloride is treated at 0° with nitrous acid, it yields a compound which from analysis and molecular weight determinations has the formula $C_8H_{10}O_2N_2$. This substance is produced by the interaction of one molecule of the base and one of nitrous acid with the elimination of two molecules of water, as indicated by the equation:

$$C_8H_{13}O_2N + HNO_2 = C_8H_{10}O_2N_2 + 2H_2O.$$

That the amino group has in this case reacted with the nitrous acid is shown by the fact that the resulting substance no longer gives a platinichloride; it must therefore be concluded that the first product of the interaction of the base and nitrous acid is a compound of the formula (IV):

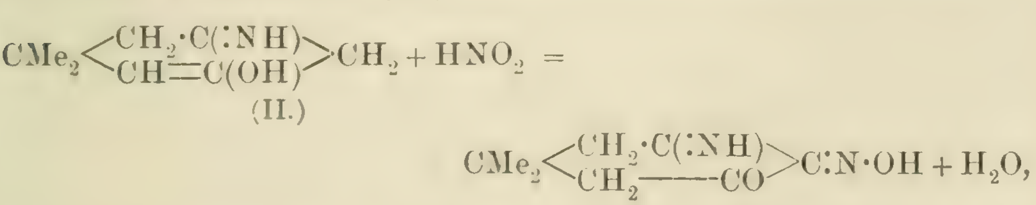


$$\begin{matrix}CMe_2\cdot CH_2\cdot C\cdot OH\\ CH_2\cdot CO—C\cdot N{:}N\cdot OH\end{matrix} \longrightarrow \begin{matrix}CMe_2\cdot CH_2\cdot C\cdot O\\ CH_2\cdot CO—C\cdot N\end{matrix}{>}N,$$

(IV.) (V.)

which, however, at once loses water, giving the substance (V), which for convenience will be referred to as compound *A*; the properties of this substance are still under investigation, and an account of them will be reserved for a subsequent communication.

The violet compound mentioned above, which is produced by the action of nitrous acid on the monoamine (II), is regarded as an *iso*nitroso-derivative of the formula (VI):



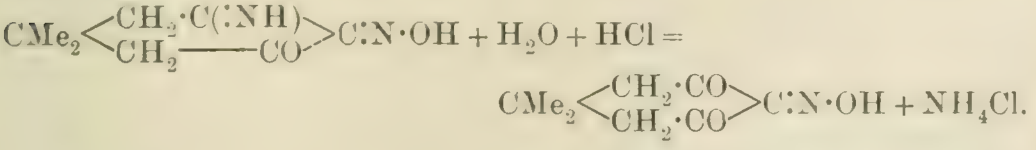
$$CMe_2{<}\begin{matrix}CH_2\cdot C({:}NH)\\ CH{=}C(OH)\end{matrix}{>}CH_2 + HNO_2 =$$

(II.)

$$CMe_2{<}\begin{matrix}CH_2\cdot C({:}NH)\\ CH_2 —— CO\end{matrix}{>}C{:}N\cdot OH + H_2O,$$

(VI.)

since on treatment with hydrochloric acid it is converted into *iso*nitrosodimethyldihydroresorcin and ammonium chloride, a fact which clearly shows that the two nitrogen atoms were not attached to each other, but to different carbon atoms:

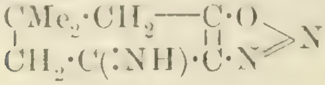


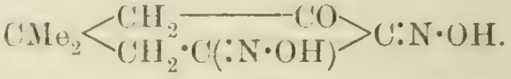
$$CMe_2{<}\begin{matrix}CH_2\cdot C({:}NH)\\ CH_2 —— CO\end{matrix}{>}C{:}N\cdot OH + H_2O + HCl =$$

$$CMe_2{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}{>}C{:}N\cdot OH + NH_4Cl.$$

Its ability to form a mono-oxime shows that, unlike the monoamine from which it was prepared, it contains a carbonyl group.

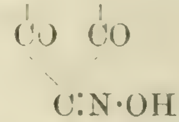
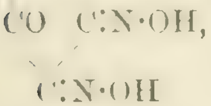
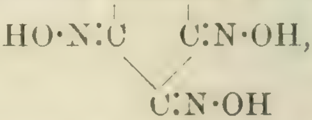
The ease with which the imino-nitrogen is split off as ammonium chloride accounts for the fact that the substance when treated with platinic chloride gives only ammonium platinichloride, and that on reduction with tin and hydrochloric acid, it is largely hydrolysed, and accordingly yields besides ammonium chloride the hydrochloride already mentioned on page 1435 as being obtained by the reduction of *iso*nitrosodimethyldihydroresorcin; in addition to these two substances, it, however, also yields a smaller quantity of another substance which would appear to be the imino-derivative of the same hydrochloride. Although this substance could not be obtained in a condition pure enough for analysis, it was found on treatment with nitrous acid to yield a substance *B*, which from its analysis and mode of preparation appears to be the imino-derivative of the substance *A* (V), and is therefore represented by the formula (VII). The same substance was also obtained by the reduction of the mono-oxime of *iso*nitrosodimethyldihydroresorcin (VIII) and the subsequent treatment of the reduction product with nitrous acid:

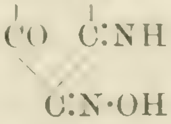
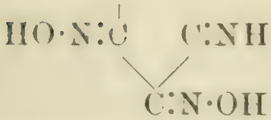

(VII.)


(VIII.)

The violet compound (VI), which is also an α-oximino-ketone, gives a magenta-coloured potassium salt, and in aqueous solution produces a deep blue colour with ferrous or ferric salts.

In this connexion it is interesting to note the influence which apparently slight changes in the constitution exert on the colour of the parent substances or of their salts.

Thus, whilst *iso*nitrosodimethyldihydroresorcin, , is yellow and its potassium and ferrous salts are blue, its mono-oxime, , is colourless, but dissolves in potassium hydroxide to form a yellow solution, and gives with ferrous sulphate a deep blue colour; its dioxime, on the other hand, , is greyish-pink, but dissolves in potassium hydroxide to give a yellow solution, and gives with ferrous sulphate in alcoholic solution a deep purple precipitate.

The replacement of one of the carbonyl groups in *iso*nitrosodimethyldihydroresorcin (III) by the imino-group changes the colour from yellow to deep violet, ; this substance gives a magenta-coloured potassium salt and a deep azure-blue ferrous salt; its oxime, on the other hand,  $\begin{array}{c}\mathrm{HO\cdot N{:}\overset{|}{C}\quad C{:}NH}\\ \diagdown\diagup\\ \mathrm{C{:}N\cdot OH}\end{array}$, is reddish-yellow, dissolves in potassium hydroxide to an orange-yellow solution, and gives a deep reddish-violet colour with ferrous sulphate.

From the above-mentioned results it must therefore be concluded that from its behaviour towards nitrous acid the constitution of the monoamine mentioned at the commencement of the paper is best represented by formula (II).

EXPERIMENTAL.

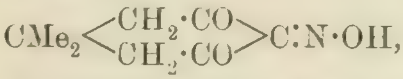
Action of Nitrous Acid on Dimethyldihydroresorcin.

Twenty grams of powdered dimethyldihydroresorcin were dissolved in a solution of 10 grams of potassium hydroxide in 60 c.c. of water; 15 grams of potassium nitrite were then added, and while the solution was cooled in a freezing mixture and thoroughly stirred by means of a turbine, concentrated hydrochloric acid diluted with an equal volume of water was slowly added; on the addition of the first drops of acid the solution turned deep blue, but as the reaction proceeded the blue colour gave way to a reddish-violet one, and a yellow, crystalline precipitate began to be formed; the concentrated hydrochloric acid was then replaced by the ordinary dilute acid, the addition being continued until the solution produced a stain with starch and potassium iodide paper. The pale yellow precipitate * was collected as rapidly as possible by the aid of the pump, washed with a little ice-cold water, and spread at once on a porous tile, when it was found to weigh 24 grams.

After recrystallisation from water, the substance was dried in a vacuum and analysed:

0·1354 gave 9·8 c.c. moist nitrogen at 16° and 755·5 mm. N = 8·39.

$C_8H_{11}O_3N$ requires N = 8·28 per cent.

iso*Nitrosodimethyldihyroresorcin*,  $\mathrm{CMe_2}\!<\!\begin{smallmatrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CO}\end{smallmatrix}\!>\!\mathrm{C{:}N\cdot OH}$, is readily soluble in alcohol, ether, or chloroform, fairly so in water, and very slightly so in light petroleum. It dissolves in water to form a pale greenish-yellow acid solution from which it crystallises in pale yellow prisms, which, when dried in a vacuum, melt with evolution of gas between 84° and 88°, according to the rate of heating. The substance is very sensitive to heat, and great care must be taken in crystallising it not to allow the temperature of the solution to rise above 50°, or else it decomposes.

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* Unless the temperature during the reaction is kept low, the resulting compound is not yellow and is decomposed largely.

The best way to proceed is to add a small quantity of the powdered substance to about ten times its weight of water, previously heated to 50°, to shake up thoroughly, and filter as rapidly as possible into a flask cooled in ice.

The solution in water has an acid reaction; on the addition of alkali the colour changes from greenish-yellow to deep blue; in aqueous solution it gives with ferrous sulphate a deep blue colour.

The *potassium* salt was prepared by adding the powdered substance to a 40 per cent. solution of potassium hydroxide gently warmed on the water-bath; the peacock-coloured, crystalline precipitate so produced was recrystallised from absolute alcohol, from which it separated in long, flat, glistening plates:

0·1404 gave 0·0624 K_2SO_4. $K = 18·76$.

$C_8H_{10}O_3NK$ requires $K = 18·84$ per cent.

The *ammonium* salt was obtained as a violet-blue oil by saturating a chloroform solution of the substance with dry ammonia, the solution being kept cool by immersion in a freezing mixture. After a short time the oil set to a heliotrope-coloured solid, which after filtration and washing with chloroform was analysed:

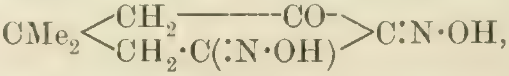
0·1234 gave 15·8 c.c. moist nitrogen at 17° and 756 5 mm. $N = 14·80$.

$C_8H_{14}O_3N_2$ requires $N = 15·05$ per cent.

The salt melts with decomposition at about 115° and dissolves readily in methyl or ethyl alcohol to a green solution, which on warming easily decomposes. If suspended in benzene and gently warmed with a few drops of methyl alcohol, a bluish-green solution is obtained, which on cooling deposits reddish-violet, prismatic plates:

0·1262 gave 16·3 c.c. moist nitrogen at 16° and 756·5 mm. $N = 14·99$.

$C_8H_{14}O_3N_2$ requires $N = 15·05$ per cent.

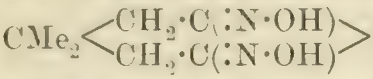
The *mono-oxime*,  $CMe_2{<}\begin{array}{l}CH_2\text{———}CO\text{-}\\ CH_2\cdot C(:N\cdot OH)\end{array}{>}C:N\cdot OH$, was obtained by adding an aqueous solution of one molecular proportion of hydroxylamine, prepared from the hydrochloride and the requisite amount of sodium carbonate, to an aqueous alcoholic solution of *iso*nitrosodimethyldihydroresorcin cooled in a freezing mixture. The solution changed colour from yellow to blue, but after a short time regained its original colour and deposited a white, crystalline precipitate, which was purified by recrystallisation from a mixture of ether and light petroleum:

0·1210 gave 15·5 c.c. moist nitrogen at 14° and 764 mm. $N = 15·15$.

$C_8H_{12}O_3N_2$ requires $N = 15·22$ per cent.

The oxime is readily soluble in cold methyl or ethyl alcohol, ethyl acetate, or acetone, fairly soluble in cold water or hot ether, slightly so in hot chloroform or benzene, and insoluble in light petroleum

(40—60°); it crystallises from a mixture of ether and light petroleum in clusters of colourless needles, and melts with evolution of gas at about 175—177° according to the rate of heating. Although quite colourless, it dissolves in alkali hydroxides to a yellow solution; in alcoholic solution, it gives with ferrous sulphate a deep blue colour.

The *dioxime*,  $CMe_2<\begin{matrix}CH_2\cdot C(:N\cdot OH)\\ CH_2\cdot C(:N\cdot OH)\end{matrix}>C:N\cdot OH$, was prepared in a similar manner to the mono-oxime, only using a slight excess over two molecular proportions of hydroxylamine; it crystallises from aqueous alcohol in stout, scaly plates of a greyish-pink colour, which melt with evolution of gas at 200—201°:

0·1178 gave 21·3 c.c. moist nitrogen at 18° and 761 mm. N = 20·92.

$C_8H_{13}O_3N_3$ requires N = 21·10 per cent.

The substance is fairly soluble in cold alcohol, less so in hot acetone, and is insoluble in ethyl acetate or water. It dissolves in potassium hydroxide to give a yellow solution, and its solution in alcohol gives with ferrous sulphate a deep purple precipitate.

Action of Oxidising Agents on iso*Nitrosodimethyldihydroresorcin.*

(*a*) *Potassium Ferricyanide.*—A solution of 2 grams of the *iso*nitroso-compound and 2 grams of potassium hydroxide in 20 c.c. of water was cooled to 4° and slowly mixed with a solution of 8 grams of potassium ferricyanide in 20 c.c. of water. The colour of the mixture turned at once from yellow to chocolate-brown; after two and a half hours, the solution was acidified and extracted with ether; on evaporating off the ether, 1 gram of a brown resin was obtained which did not crystallise. That oxidation had taken place was shown by the heavy Prussian-blue precipitate which was formed on adding a little ferric chloride to the ferricyanide mixture.

(*b*) *Hydrogen Peroxide.*—Thirty c.c. of hydrogen peroxide (20 vols.) were added during the course of two hours in portions of 10 c.c. at a time to a solution of 2 grams of *iso*nitroso-compound and 2 grams of potassium hydroxide in 15 c.c. of water. After twenty-four hours, the solution was acidified; a slight effervescence due to the escape of carbon dioxide and oxides of nitrogen was observed. The solution was extracted four times with ether and the ethereal extract after drying and evaporating left 1·2 grams of a yellow, oily residue containing some crystals; this residue was identified as ββ-dimethylglutaric acid by converting it into its anhydride which melted at 124·5°; the anhydride was then further converted into the anilide which after recrystallising from aqueous alcohol melted at 134°.

(*c*) *Oxides of Nitrogen.*—Two grams of *iso*nitrosodimethyldihydroresorcin were dissolved in ether and the solution was saturated with oxides of nitrogen obtained by heating arsenious oxide with 50 per cent. nitric acid. The solution at first turned dark brown, but gradually became lighter in colour and slightly warm; shortly after the space in the flask above the ether became filled with brown fumes; the passage of the oxides of nitrogen was then interrupted and the ether was rapidly evaporated by driving a current of air through the solution. The light yellow, oily residue which remained was then mixed with a little water, cooled in a freezing mixture, and rapidly stirred; 1·5 grams of a crystalline solid were obtained which were recrystallised from a mixture of benzene and light petroleum:

0·1156 gave 0·2193 CO_2 and 0·0678 H_2O. $C = 51·73$; $H = 6·51$.
0·1210 ,, 8·2 c.c. moist nitrogen at 15° and 744 mm. $N = 7·76$.
$C_8H_{11}O_4N$ requires $C = 51·88$; $H = 5·94$; $N = 7·57$ per cent.

This substance, which is nitrodimethyldihydroresorcin, was subsequently prepared more easily from dimethyldihydroresorcin, and an account of its preparation from that source and of its properties will be found on page 1441.

Action of Reducing Agents on iso*Nitrosodimethyldihydroresorcin.*

(*a*) *Aluminium Amalgam.*—Two grams of the *iso*nitroso-compound were dissolved in alcohol and left for three hours in contact with aluminium amalgam made from 2 grams of aluminium, small quantities of water being added from time to time; on filtering the solution and evaporating it to dryness in a vacuum, a brown mass remained behind which weighed 1·3 grams. The substance could not be further purified.

Similar experiments, using ether as a solvent in place of alcohol, likewise led to no definite conclusion, the resulting substance having a decomposed appearance and being uncrystallisable.

(*b*) *Tin and Hydrochloric Acid.*—An experiment in which the *iso*nitroso-compound was reduced with tin and concentrated hydrochloric acid resulted in the complete decomposition of the whole substance owing to the mixture becoming a little warm from the reaction.

(*c*) *Ammonium Sulphide.*—A solution of 4 grams of the *iso*nitroso-compound in an aqueous solution of ammonia was saturated with hydrogen sulphide; after some time it was acidified, filtered, and evaporated over a water-bath; the residue consisted chiefly of ammonium chloride together with a small quantity of some other substance which was, however, not identified. A number of other experiments under slightly altered conditions having been performed without yielding any pure substance, the reduction product was treated with nitrous acid in the hope of obtaining a crystalline derivative. For this purpose, 3·5 grams of the *iso*nitroso-compound were dissolved in aqueous ammonia, and after saturating with hydrogen sulphide the solution was filtered; the filtrate after acidification was evaporated somewhat, and treated with a solution of potassium nitrite until it reacted with starch and potassium iodide paper. A pale brown precipitate was formed which weighed 1·2 grams; after recrystallisation from a mixture of ether and light petroleum, the substance melted at 105—107° with evolution of gas:

0·1320 gave 0·2784 CO_2 and 0·0741 H_2O. C = 57·52; H = 6·23.
0·1340 ,, 0·2834 CO_2 ,, 0·0756 H_2O. C = 57·67; H = 6·29.
0·1504 ,, 22 c.c. moist nitrogen at 20° and 761·2 mm. N = 16·76.
$C_8H_{10}O_2N_2$ requires C = 57·83; H = 6·02; N = 16·86 per cent.
$C_8H_{12}O_2N_2$,, C = 57·14; H = 7·14; N = 16·66 ,,

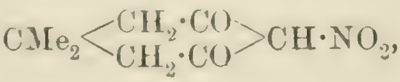
This substance *A* was subsequently obtained more readily from aminodimethyldihydroresorcin, and an account of its preparation from that source will be found on page 1444.

Action of Oxides of Nitrogen on Dimethyldihydroresorcin.

Thirty grams of dimethyldihydroresorcin were finely powdered and suspended in 250 c.c. of ether contained in a conical flask; into this were conducted the brown fumes evolved by gently warming 100 grams of arsenious oxide with about 100 grams of concentrated nitric acid diluted with an equal quantity of water. The ether assumed a brown colour which gradually darkened as the suspended dimethyldihydroresorcin dissolved; a little time after the whole of it had gone into solution, the liquid became lighter in colour; the passage of the gas was then interrupted and the ethereal solution was rapidly evaporated by blowing a current of air through it. After evaporating down to about 90 c.c., 20 grams of crystals separated. On adding light petroleum to the mother liquors, an oil was precipitated which, however, on cooling in a freezing mixture and stirring, set to a mass of crystals which weighed 12 grams. The total yield of solid was accordingly 32 grams. Attempts to evaporate off the ether over a water-bath resulted in a very violent evolution of oxides of nitrogen and a considerable amount of decomposition. Prepared as above, the substance is sufficiently pure to be employed directly for further reactions, but if it is to be kept for some time it should be recrystallised, as the impure substance gradually softens and becomes sticky. Analysis of a sample recrystallised from a mixture of ether and light petroleum gave the following numbers:

0·1263 gave 8·5 c.c. moist nitrogen at 13° and 755 mm. N = 7·88.
$C_8H_7O_4N$ requires N = 7·57 per cent.

4-*Nitro*-1:1-*dimethyldihydroresorcin*,



$$CMe_2<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>CH\cdot NO_2,$$

crystallises from a mixture of ether and light petroleum in colourless, glistening, prismatic plates; if heated rapidly on platinum foil it melts without decomposition and resolidifies on cooling; if heated slowly in a capillary tube it turns brown and melts with evolution of gas at 100—102°; it is very readily soluble in cold methyl or ethyl alcohol, ethyl acetate, ether, chloroform, or benzene, but is insoluble in light petroleum. It dissolves fairly readily in cold water and in potassium or ammonium hydroxide to form yellow solutions; its aqueous solution, which has an acid reaction, gives with ferrous sulphate a reddish-brown, and with ferric chloride a bright yellowish-red, colour.

The *ammonium* salt was prepared by dissolving 2 grams of nitrodimethyldihydroresorcin in 5 c.c. of concentrated ammonia solution and evaporated to small bulk over a water-bath. The salt separated in light amber-coloured crystals, which were recrystallised from a mixture of alcohol and light petroleum:

0·1292 gave 0·2242 CO_2 and 0·0841 H_2O. $C = 47·32$; $H = 7·23$.

0·1214 ,, 14 c.c. moist nitrogen at 9° and 775 mm. $N = 14·15$.

$C_8H_{14}O_4N_2$ requires $C = 47·52$; $H = 6·93$; $N = 13·86$ per cent.

The salt is readily soluble in cold ethyl acetate or hot ethyl alcohol, is only very slightly soluble in hot acetone, and is insoluble in chloroform, benzene, or light petroleum; it crystallises from a mixture of alcohol and light petroleum in stellar aggregates of rhombic plates and melts with evolution of gas at 187·5—188·5°, but begins to contract some degrees below this temperature; its aqueous solution has a neutral reaction.

The *potassium* salt was obtained as a pale yellow oil on adding nitrodimethyldihydroresorcin to a 40 per cent. potassium hydroxide solution warmed on a water-bath. On cooling, the oil solidified and was purified by twice recrystallising from alcohol:

0·1636 gave 0·0584 K_2SO_4. $K = 16·02$.

0·1685, on heating to 105°, lost 0·0136. $H_2O = 8·07$.

$C_8H_{10}O_4NK,H_2O$ requires $K = 16·18$; $H_2O = 7·47$ per cent.

Analysis of the substance dried at 105° gave the following numbers:

0·1524 gave 0·0592 K_2SO_4. $K = 17·44$.

$C_8H_{10}O_4NK$ requires $K = 17·49$ per cent.

The salt crystallises in lemon-yellow, silken needles and decomposes with explosive violence when rapidly heated on platinum foil. When heated in a capillary tube it dissolves in its own water of crystallisation at about 80°, evolves water below 100°, becoming solid again and melting to a brown liquid at about 230°. Its aqueous solution is bright yellow and is neutral to litmus.

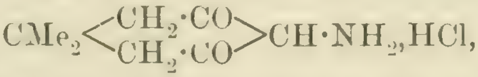
Reduction of Nitrodimethyldihydroresorcin to Aminodimethyldihydroresorcin.

Fifteen grams of granulated tin were gradually added to a mixture of 10 grams of nitrodimethyldihydroresorcin with 30 grams of concentrated hydrochloric acid ; the mixture was repeatedly shaken and cooled under water in order to moderate the reaction ; 3 grams more of tin were then added, and the whole was set aside overnight The reddish-brown liquid so obtained was then filtered, and after largely diluting with water was saturated while hot with hydrogen sulphide ; after filtering off the stannous sulphide, the solution, which had a very disagreeable odour resembling that of bitter aloes, was evaporated on a water-bath to about 90 c.c. ; on cooling, clusters of pale reddish-yellow crystals were deposited, which after recrystallisation from a mixture of alcohol and ether gave the following numbers on analysis :

0·1279 gave 8 c.c. moist nitrogen at 12° and 773·5 mm. N = 7·55

$C_8H_{13}O_2N,HCl$ requires N = 7·31 per cent.

4-*Amino*-1 : 1-*dimethyldihydroresorcin hydrochloride*,



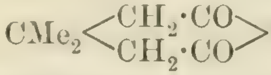
$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CO}\end{matrix}\!>\!\mathrm{CH\cdot NH_2,HCl},$$

is readily soluble in water or ethyl alcohol, but is insoluble in other organic solvents.

The *platinichloride*, $(C_8H_{13}O_2N)_2,H_2PtCl_6$, was obtained by mixing together alcoholic solutions of the hydrochloride and platinic chloride ; after evaporating some of the alcohol and largely diluting with ether, the salt was deposited in yellow, prismatic crystals ; it is readily soluble in alcohol or water, and is somewhat hygroscopic ; for analysis it was finely powdered and dried in a vacuum :

0·2233 gave 0·0600 Pt. Pt = 26·87.

$C_{16}H_{28}O_4N_2Cl_6Pt$ requires Pt = 27·08 per cent.

The *acetyl* derivative,  $\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CO}\end{matrix}\!>\!\mathrm{CH\cdot NHAc}$, was prepared by heating 1·7 grams of the hydrochloride over a water-bath for three-quarters of an hour with a mixture of 2·5 grams of acetic anhydride and 2·5 grams of acetyl chloride. The mixture was then evaporated with methyl alcohol, when it left a pale brown, solid residue which, after drying in a vacuum, was repeatedly extracted with light petroleum. The extract on evaporation yielded 0·7 gram of pure white, prismatic needles, which melted at 115—116° :

0·1264 gave 0·2847 CO_2 and 0·0932 H_2O. C = 61·42 ; H = 8·18.

0·1418 ,, 8·5 c.c. moist nitrogen at 15° and 779·5 mm. N = 7·21.

$C_{10}H_{15}O_3N$ requires C = 60·91. H = 7·61 ; N = 7·10 per cent.

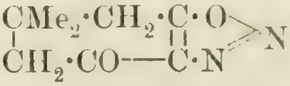
$C_{10}H_{17}O_3N$,, C = 60·30. H = 8·54 ; N = 7·03 ,, ,,

Action of Nitrous Acid on Aminodimethyldihydroresorcin.

Eight grams of aminodimethyldihydroresorcin hydrochloride dissolved in 40 c.c. of water were mixed with 3·5 grams of concentrated hydrochloric acid and cooled in a freezing mixture; a solution of 4 grams of potassium nitrite in 30 c.c. of water was then added drop by drop until a permanent reaction with starch and potassium iodide paper was obtained. The pale buff-coloured, crystalline precipitate thus produced was collected, washed with water, and dried, when it weighed 5·7 grams. On extracting the filtrate with ether, a little more of the same substance was obtained. After recrystallisation from a mixture of alcohol and light petroleum, it melted at 107—108° with evolution of gas, and was found to be in every respect identical with the substance *A* obtained by the action of nitrous acid on the reduction product of *iso*nitrosodimethyldihydroresorcin (page 1441):

0·1231 gave 17·8 c.c. moist nitrogen at 14° and 774 mm. N = 17·32.
$C_8H_{10}O_2N_2$ requires N = 16·86 per cent.

This substance *A*, the constitution of which may be represented by the formula



$$\begin{array}{l}\mathrm{CMe_2{\cdot}CH_2{\cdot}C{\cdot}O} \\ \mathrm{CH_2{\cdot}CO{-\!-}C{\cdot}N}\end{array}\!\!>\!\mathrm{N}$$

, is readily soluble in alcohol, acetone, ethyl acetate, chloroform, ether, or benzene, and crystallises in long, yellow prisms from light petroleum (40—60°) or from a mixture of this solvent with alcohol. It is somewhat soluble in water, and dissolves in potassium hydroxide to a pale yellow solution; it may be recovered unchanged after evaporation on a water-bath with a solution of ammonia or of dilute or concentrated hydrochloric acid; its alcoholic solution gives no colour with either ferrous or ferric salts, but attempts to prepare from it either an oxime or a semicarbazone were unsuccessful.

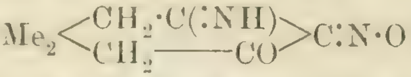
The molecular weight was determined by the freezing point method, using naphthalene as solvent:

0·2998 in 19·0282 naphthalene gave Δt – 0·641. M.W. = 168.
0·6467 ,, ,, ,, ,, Δt – 1·369. M.W. = 171.
$C_8H_{10}O_2N_2$ requires M.W. = 166.

Action of Nitrous Acid on Iminohydroxydimethyldihydrobenzene.

Thirteen grams of the crude base (II), obtained by evaporating to dryness a solution of dimethyldihydroresorcin in ammonium hydroxide, were finely powdered and suspended in a solution of 9 grams of potassium nitrite in 50 c.c. of water. While cooled in a freezing mixture, the liquid was stirred by means of a mechanical stirrer and treated with a solution of 13 grams of concentrated hydrochloric acid in an equal volume of water until the mixture gave a permanent reaction with starch and potassium iodide paper; the heliotrope-coloured solid was then rapidly collected by the aid of the pump, washed with 25 c.c. of cold water, pressed on a porous tile, and found to weigh about 20 grams. It was recrystallised in two separate portions by adding 10 grams of the roughly-powdered substance to 120 c.c. of boiling alcohol, boiling for a few seconds, and rapidly filtering through a heated funnel into a flask cooled in ice. In this way altogether about 8 grams of pure substance were obtained:

0·1361 gave 0·2871 CO_2 and 0·0927 H_2O. C = 57·53; H = 7·56.
0·1441 „ 0·3020 CO_2 „ 0·1038 H_2O. C = 57·15; H = 8·00.
0·1177 „ 16·6 c.c. moist nitrogen at 14 and 761·5 mm. N = 16·62.
0·1248 „ 17·8 c.c. „ „ „ 19° „ 771 mm. N = 16·64.
$C_8H_{12}O_2N_2$ requires C = 57·14; H = 7·14; N = 16·6 per cent.

4-*Oximino*-3-*imino*-1 : 1-*dimethyl*cyclo*hexane*-5-*one* (referred to for convenience as the violet compound),  $CMe_2\left\langle\begin{array}{l}CH_2\cdot C(:NH)\\ CH_2\text{———}CO\end{array}\right\rangle C:N\cdot OH$, crystallises from alcohol in violet-blue, lustrous scales which do not melt, but on heating gradually darken in colour and suddenly char and evolve a quantity of orange-coloured fumes; it is insoluble in most ordinary organic solvents except alcohol; it may be recrystallised from water also, but owing to the higher boiling point of this solvent it is not so suitable as alcohol, inasmuch as the substance readily decomposes when its solution is heated. It is important that the crude substance be recrystallised at once, as otherwise slight decomposition sets in, the violet-blue colour turning gradually brownish-violet, and it is then impossible to restore the original colour by recrystallisation. The pure solid may be kept for a considerable time without showing any signs of decomposition, but its solutions decompose fairly readily even in the cold and rapidly on warming.

The solution in water is neutral to litmus and has a violet-blue colour which changes to a deep azure-blue on the addition of an iron salt, but is unchanged by the addition of alkali. When a solution of the substance in one molecular proportion of hydrochloric acid is evaporated in a vacuum, it loses its blue colour and deposits a mass of pale yellow needles, which on dissolving in ether leave a residue of ammonium chloride; the ethereal solution treated with light petroleum gave crystals of *iso*nitrosodimethyldihydroresorcin which were identified by their melting point and by the fact that they did not depress the melting point of the pure substance.

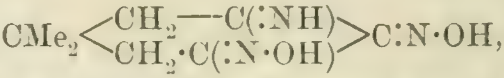
The ease with which the substance loses one atom of nitrogen in the form of ammonium chloride when treated with hydrochloric acid accounts for the fact that with platinic chloride and hydrochloric acid it gives only the ammonium salt of chloroplatinic acid.

The *potassium* salt was prepared by shaking up the finely-powdered substance with 40 per cent. potassium hydroxide, when the violet colour changed at once to a bright magenta. The solid was collected and recrystallised by dissolving in the least possible quantity of alcohol and diluting the solution with a very large volume of chloroform, when it was obtained in stellar aggregates of long, slender plates which melt with decomposition at about 82°:

0·1487 gave 0 0616 K_2SO_4. $K = 18·60$.

$C_8H_{11}O_2N_2K$ requires $K = 18·93$ per cent.

The salt is very hygroscopic and on exposure to the air it absorbs carbon dioxide and rapidly darkens in colour, ultimately becoming blue and being much less soluble in alcohol. On extracting the blue solid with hot alcohol, an insoluble residue of potassium carbonate was obtained, the alcoholic solution on evaporation yielding crystals of the violet compound.

To prepare the *oxime*,  $CMe_2\left<\begin{array}{l}CH_2\text{—}C(:NH)\\CH_2\cdot C(:N\cdot OH)\end{array}\right>C:N\cdot OH$, 2 grams of the violet compound were suspended in 50 c.c. of alcohol and mixed with an aqueous solution of 1 gram of hydroxylamine hydrochloride and 0·6 gram of sodium carbonate; the clear reddish-brown solution so obtained was warmed for twenty minutes on a water-bath and then evaporated to a small bulk, when a reddish-yellow solid was obtained which after recrystallising from aqueous alcohol melted at 196—197°:

0·1284 gave 25·2 c.c. moist nitrogen at 17° and 771·5 mm. $N = 23·12$.

$C_8H_{13}O_2N_3$ requires $N = 22·95$ per cent.

It is readily soluble in alcohol, ethyl acetate, or acetone, insoluble in chloroform, ether, or light petroleum, but is slightly soluble in water; its aqueous solution gives with ferrous sulphate a deep reddish-violet colour; it dissolves in potassium hydroxide to an orange-yellow solution.

Reduction of 4-*Oximino*-3-*imino*-1 : 1-*dimethyl*cyclo*hexane*-5-*one* (the violet compound).

Five grams of the violet compound suspended in 15 grams of concentrated hydrochloric acid were gradually treated with 9 grams of metallic tin, the temperature of the mixture not being allowed to rise above 15°. After twelve hours, the brown solution was largely diluted with water, and, after removing the tin with hydrogen sulphide, was evaporated to a small bulk on a water-bath and finally to dryness in a vacuum. On extracting the residue with alcohol, a brown solution was obtained, which was filtered from a quantity of ammonium chloride and evaporated to small bulk; on largely diluting with chloroform, the solution deposited a buff-coloured, crystalline precipitate of the hydrochloride of aminodimethyldihydroresorcin described on page 1443:

0·1068 gave 6·8 c.c. moist nitrogen at 20° and 753 mm. N = 7·21.

$C_8H_{14}O_2NCl$ requires N = 7·31 per cent.

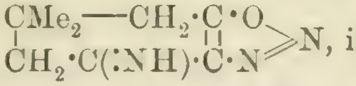
After several unsuccessful attempts to isolate any other pure substance from the reduction product, a fresh quantity of 5 grams of material was reduced, and the solution obtained after the removal of the tin was evaporated to small bulk, cooled in a freezing mixture, and treated with a solution of potassium nitrite until a permanent starch and potassium iodide reaction was obtained. The solution deposited 0 7 gram of a crystalline solid, and a further quantity of the same material was obtained from the solution by extracting with ether; the two quantities were put together and recrystallised from alcohol, when the solution deposited colourless, glistening plates which melted at 203—205° with evolution of gas:

0·1218 gave 0·2588 CO_2 and 0·0786 H_2O. C = 57·94; H = 7·17.

0·1160 ,, 24·7 c.c. moist nitrogen at 14° and 778 mm. N = 25·65.

$C_8H_{11}ON_3$ requires C = 58·18; H = 6·66; N = 25·45 per cent.

$C_8H_{13}ON_3$,, C = 57·48; H = 7·78; N = 25·15 ,,

This substance *B*,  $\begin{array}{l} CMe_2\text{—}CH_2\cdot C\cdot O \\ CH_2\cdot C(:NH)\cdot C\cdot N \end{array}\!\!>\!N$, is readily soluble in cold alcohol, acetone, ethyl acetate, or ether, fairly so in hot water, slightly so in chloroform or ether, and is insoluble in light petroleum.

Its *platinichloride*, $(C_8H_{11}ON_3)_2,H_2PtCl_6$, was obtained as an oil by allowing an alcoholic solution of 0·5 gram of substance and 0·6 gram of platinic chloride to evaporate slowly; on stirring the oil after some days with water, it solidified, and after washing with water and drying gave the following numbers on analysis:

0·1931 gave 0·0522 Pt. Pt = 27·03.

$C_{16}H_{24}O_2N_6Cl_6Pt$ requires Pt = 26·35 per cent.

The alcoholic mother liquors of the substance *B* on treatment with light petroleum gave needle-shaped crystals which melted at 105—107°, and were identical with the substance *A* of the same melting point described on page 1444, showing that when the violet compound is reduced in hydrochloric acid solution, part of it is reduced as such and part of it undergoes hydrolysis, losing the imino-group in the form of ammonium chloride, and giving the hydrochloride of aminodimethyldihydroresorcin; consequently, when the resulting mixture is treated with nitrous acid, a mixture of the substance *A* and its imino-derivative *B* is obtained.

Reduction of the Oxime of iso*Nitrosodimethyldihydroresorcin.*

Four grams of the oxime dissolved in 13 grams of concentrated hydrochloric acid were treated with 5 grams of metallic tin, which were added in portions, the temperature during the reaction being kept below 15°. After twelve hours, the mixture had set to a brown, semi-solid mass, most of which, however, dissolved on largely diluting with water. After filtering from a small quantity of undissolved tin, the brown solution was heated over a boiling water-bath and then saturated with hydrogen sulphide; on filtering off the sulphide of tin, the solution was concentrated to about 60 c.c.; it was then cooled in a freezing mixture and treated with a solution of potassium nitrite until it gave a permanent reaction with starch-iodide paper; a crystalline precipitate weighing 0·7 gram was obtained, and the solution on extraction with ether yielded a further quantity of the same substance; after recrystallisation from a mixture of alcohol and light petroleum, this substance melted at 203·5—204·5° and was shown to be identical with the substance *B* by the fact that when mixed with this substance it did not depress its melting point.

In conclusion, the author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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CXXXVIII.—*The Action of Hydrogen Peroxide on Potassium Cyanide.*

By Orme Masson, D.Sc., F.R.S.

The formation of oxamide by the action of hydrogen peroxide on hydrocyanic acid was discovered in 1863 by Attfield (*Journ. Chem. Soc.*, 1863, **16**, 94). Radziszewski afterwards (*Ber.*, 1885, **18**, 355) showed that oxamide is only one of the products of an apparently complex change and that its formation is very slow, but he found that cyanogen in the presence of a trace of potassium cyanide is rapidly and quantitatively converted into oxamide by hydrogen peroxide.

The rate with which potassium cyanide disappears under the influence of hydrogen peroxide was investigated by C. J. Martin and R. A. O'Brien (*Proc. Soc. Chem. Ind. Victoria*, 1901, 1, 119). The curves obtained, whilst sufficient for the purpose the authors had in view, are irreconcilable with any simple theory of oxidation, and their investigation left the real nature of the reaction and its products unexplained. It seemed likely that results of interest might be obtained by combining analyses of the finished product with titration both of the residual cyanide and of the residual peroxide during the course of the action. An account of the work done on these lines is given in the sequel.

The Nature of the Action.

When aqueous solutions of potassium cyanide and hydrogen peroxide are mixed, the action at first proceeds quietly and without gas evolution, but with rise of temperature, which, if it be not counteracted by cooling precautions, may soon cause the action to be completed with almost explosive violence. If solutions containing 2 or more gram-molecules per litre are to be mixed in any considerable quantity, careful ice-cooling is required to prevent the action from getting beyond control, but in the case of solutions of 1 gram-molecule per litre or less, the heating effect is practically counteracted by immersing the mixing vessel in a bath of water at the ordinary temperature.

In this action, oxamide crystals are never produced; they are, however, formed in small quantity if the peroxide is mixed beforehand with sulphuric acid equivalent in amount to the potassium cyanide, but they have not been observed when smaller amounts of acid are used, nor when neutral peroxide is added in any proportion to potassium cyanide. It seems, therefore, that Attfield's action does not occur unless the mixture is actually acid to indicators. Ordinary commercial preparations of peroxide may give rise to white precipitates in the course of the action with cyanide, but these are derived from inorganic impurities in the peroxide itself. They are generally amorphous, but in some cases crystals have been obtained which might be mistaken for oxamide on casual inspection, but which turned out on analysis to be magnesium ammonium phosphate. With pure peroxide (Merck's) there is never any trace of solid matter formed, the solution remaining clear and colourless from first to last. Not only is oxamide entirely absent, but tests for soluble oxalate also give negative results when applied to the mixed solution after action is complete.

The main products of the action are potassium cyanate and potassium and ammonium carbonates. Of these, the former seems to be the primary product, whilst the latter probably results from a secondary hydrolytic action in which hydrogen peroxide acts as a catalyst:

$$(1)\quad KCN + H_2O_2 = KCNO + H_2O.$$

$$(2)\quad KCNO + 2H_2O = K(NH_4)CO_3.$$

Taken together, the cyanate and carbonate are found to account for approximately four-fifths of the original cyanide and an equimolecular quantity of peroxide. The balance of the cyanide (one-fifth) is never oxidised, even though a large excess of peroxide be employed, but is converted by hydrolysis into potassium formate and ammonia, and in this action also the peroxide plays the part of a catalytic agent:

$$(3)\quad KCN + 2H_2O = H{\cdot}CO_2K + NH_3.$$

No free oxygen is produced during the action so long as any appreciable amount of cyanide remains unchanged, but as soon as it has disappeared there sets in a decomposition of the remaining peroxide, which will be present if the original molecular ratio of the peroxide to the cyanide exceeded about 4 : 5. This decomposition, which causes a brisk escape of oxygen, is practically completed in a few hours at the ordinary temperature, and is evidently due to the catalytic influence of one or more of the substances derived from the cyanide.

The solution ultimately obtained contains, therefore, no peroxide and no cyanide, unless the latter was present in too large an excess at the start, but it contains the oxidation and hydrolysis products of the reactions already mentioned.

Materials and Analytical Methods.

The hydrogen peroxide used in all the experiments recorded, except those of Tables II and III, was Merck's pure 30 per cent., diluted as required. The crystallised potassium cyanide employed was found to be free from impurities except a trace of carbonate. The solutions were made up with distilled water, which was boiled and cooled immediately before use.

Determinations of cyanide were made by titration with standard silver nitrate after adding a little potassium hydroxide and potassium iodide. This precaution is necessary in testing after or during the peroxide action, as ammonia is one of its products. It was proved that the accuracy of the method is not otherwise interfered with.

Determinations of peroxide were made by titration with standard potassium permanganate in presence of excess of sulphuric acid. It was proved by special tests that neither cyanide, as such, nor formate spoils the accuracy of the indications.

In the solutions containing the products of the action, the carbonate was determined by precipitating a measured volume with excess of barium nitrate and weighing the washed and ignited barium carbonate.

The cyanate was determined in the filtrate from the barium carbonate by adding excess of silver nitrate and sufficient very dilute nitric acid to neutralise exactly the free ammonia present. The silver cyanate was ignited and weighed as silver.

The formate was detected by mixing the product with dilute sulphuric acid, boiling off the carbon dioxide, and distilling; for quantitative purposes a modification of Lieben's method was used. Preliminary tests proved the accuracy of this method when applied to formate solutions made from pure formic acid, but the results obtained by it in the present investigation are less satisfactory, although every care was taken to ensure accuracy. The formate so determined generally fell rather short of the amount expected as the result of other methods of inquiry, which will be described later. The cause of the discrepancy has not been ascertained.

Free ammonia could always be detected during the progress of the action. The quantity found by titration at the end was variable and was always less than the equivalent of the formate; this being doubtless due to loss by evaporation.

The Final Products of the Action.

The analyses summarised in Table I were all made with residual solutions at the conclusion of velocity experiments to be described later; and in each case, except where recorded, the complete previous destruction of both peroxide and cyanide was proved. Each result recorded is the mean of two or more determinations, which were always closely concordant in the cases of carbonate and cyanate, although less so in those of formate. All results are reduced to a uniform basis by referring them to one molecule of original potassium cyanide, but the actual initial strengths of potassium cyanide and hydrogen peroxide in gram-molecules per litre are given in the second and third columns. The values given in the last column, under the heading "hydrolysed," are obtained from the velocity curves, as will be explained later, and agree well with those in the preceding column, which shows the difference between the cyanide destroyed and the amount represented by the carbonate and cyanate found. These values are probably more trustworthy than the direct determinations of formate.

Table I.—*Action of* H_2O_2 *on* KCN *in Aqueous Solution at* 20°.

	Gram-mol. per litre in original mixture.		Ratio	Fraction of original CN found finally as						
			of H_2O_2						Hydrolysed.	
No of expt.	H_2O_2.	KCN.	to KCN.	Cyanide, CN.	Cyanate, CNO.	Carbonate, CO_3.	Formate, CHO_2.	Total oxidised.	(Diff.).	(Curve).
I.	0·477	0·483	0·988	0	0·331	0·454	0·201	0·785	0·215	0·22
II.	0·240	0·240	1·000	0	0·290	0·490	0·150	0·780	0·220	0·20
III.	0·127	0·125	1·016	0	0·402	0·416	0·155	0·818	0·182	0·17
IV.	0·299	0·248	1·206	0	0·229	0·568	0·190	0·797	0·203	0·20
V.	0·254	0·248	1·024	0	0·324	0·455	0·182	0·779	0·221	0·20
VI.	0·204	0·249	0·819	0	0·447	0·339	0·189	0·786	0·214	0·21
VII.	0·196	0·251	0·781	trace	0·459	0·332	0·203	0·791	0·209	0·21
VIII.	0·149	0·248	0·601	0·207	0·430	0·193	—	0·623	0·170	0·18

It may be noted that carbamide does not figure among the products of oxidation, although it might be expected to occur in a solution containing both cyanic and ammonium ions. But the formation of carbamide is a very slow process at the ordinary temperature, and these solutions were not raised above 20°, and were analysed without delay. Any undetected traces of carbamide which may have been present would, if allowed for, tend slightly to raise the estimate of total oxidation and correspondingly lower the estimate of hydrolysis by difference. The error arising from the trace of carbonate in the original cyanide, which would tend in the opposite direction, was proved to be very small.

A study of Table I leads to the following conclusions. The amount of carbonate produced per molecule of original cyanide depends mainly on the original ratio of peroxide to cyanide, increasing with it, although not in simple proportionality. The cyanate decreases as the carbonate increases, so that their sum, or the total fraction of the original cyanide which has undergone oxidation, remains nearly constant at about 0·79. It seems likely, as already suggested, that the cyanate is the primary product of the oxidation process, and that its natural tendency to form carbonate by hydrolysis is catalytically accelerated by hydrogen peroxide. The unaided hydrolysis is very slow, for cyanate solutions may be kept nearly unchanged for a long time.

The ratio of total oxidation (cyanate plus carbonate) to original cyanide is but slightly affected by comparatively large changes in the initial concentration of the latter, and appears to be quite independent of the initial ratio of hydrogen peroxide to potassium cyanide, so long as this is not less than the requisite minimum of about 4 to 5. The same rule applies to the unoxidised or hydrolysed fraction, which is roughly one-fifth of the original. Other evidence for this conclusion will be dealt with later.

All of the peroxide which is not used for oxidation of cyanide, namely, all originally present in excess of the 4 to 5 ratio, is represented ultimately by free oxygen, as already mentioned. Accurate measurements of the gas evolved cannot be made unless the solution be confined over mercury, as errors arise from supersaturation and other causes. The following experiments were therefore made with small quantities of material confined over mercury in a nitrometer at the laboratory temperature. The materials used were not quite so pure as those employed in the rest of the work recorded in this paper, but experience has shown that practically identical results are obtained with cyanide and peroxide from various sources.

The nitrometer having been filled with mercury, small measured volumes of potassium cyanide and hydrogen peroxide solutions of known strengths were admitted and washed in with measured volumes of water, and the whole mixed by shaking. No oxygen was formed at first, the time elapsing before its appearance varying with the composition of the solution. When, after several hours, the evolution appeared to be complete, the dissolved gas was pumped out by lowering the mercury column, and measurements were made of volume, pressure, and temperature. This was repeated at intervals of an hour or so until the result was constant. The volume so obtained was reduced to 0° and 760 mm., with a correction for moisture, and the equivalent of hydrogen peroxide was calculated. As examination of the residual solution proved it to be quite free from hydrogen peroxide, as well as from potassium cyanide, the difference between the original hydrogen peroxide and the equivalent of the free oxygen so calculated may obviously be put down as peroxide reduced by the cyanide, or (since the reaction is an equimolecular one) as potassium cyanide oxidised. It should be stated that the gas evolved during the action was in several cases proved by analysis to be pure oxygen.

In the following table the results of the actual experiments have been reduced to the basis of one molecule of original cyanide. The strengths and volumes used differed in each case, but it was always arranged that the mixture should contain from one-fifth to one-half of a gram-molecule of each reagent per litre.

TABLE II.—*Nitrometer Tests with* H_2O_2 : KCN *greater than* 1.

Mols. of H_2O_2 used per KCN.	H_2O_2 equiv. of O_2 gas obtained.	Balance of H_2O_2 = KCN oxidised.	Balance of KCN = KCN hydrolysed.
2·5	1·71	0·79	0·21
2·25	1·46	0·79	0·21
2·0	1·22	0·78	0·22
1·75	0·98	0·77	0·23
1·5	0·72	0·78	0·22
1·33	0·54	0·79	0·21
1·0	0·22	0·78	0·22
1·0	0·22	0·78	0·22

It is evident that approximately 0·78 of the original potassium cyanide is oxidised to cyanate and carbonate and 0·22 hydrolysed to formate, and that the whole of the unused peroxide is converted into water and free oxygen; also that these results are independent of the initial ratio of peroxide to cyanide, at least within the limits cited. This confirms the conclusions already based on other evidence.

The experiments cited in the next table were conducted similarly, but with mixtures containing less than one molecule of peroxide to one of cyanide. In each case the complete destruction of the peroxide was proved by titration with permanganate, and the surviving cyanide was detected and determined by titration with silver nitrate. No appreciable free oxygen was formed, so that the whole of the peroxide was used in oxidising the cyanide to cyanate and carbonate. The cyanide simultaneously destroyed by hydrolysis is necessarily the difference between the original quantity and the sum of that oxidised and that surviving unchanged. The results show that this hydrolysis still bears the same ratio to the original (a little over one-fifth) until the initial H_2O_2 : KCN ratio falls below 0·5, after which it gradually diminishes. In the only previously quoted experiment bearing on this point (VIII of Table I) some diminution was observed when this ratio was 0·6, but there the temperature was somewhat higher and the action quicker.

TABLE III.—*Nitrometer Tests with* H_2O_2 : KCN *less than* 1.

Mols. of H_2O_2 used per KCN.	H_2O_2 equiv. of free O_2.	Unchanged KCN found.	KCN oxidised.	KCN hydrolysed.
1·0	0·21	0·00	0·79	0·21
0·67	0·01	0·13	0·66	0·21
0·5	0·02	0·31	0·48	0·21
0·5	0·0	0·30	0·50	0·20
0·4	0·0	0·42	0·40	0·18
0·33	0·0	0·51	0·33	0·16

Study of the Action in Progress.

That cyanide should be partly oxidised to cyanate and carbonate and partly hydrolysed to formate when exposed to the action of hydrogen peroxide, and that the excess of peroxide should undergo decomposition into water and oxygen seem in no way remarkable; but that the ratio of oxidation to hydrolysis, or of either to the total cyanide, should be so nearly independent of the absolute and relative concentrations of the reagents is somewhat surprising. Moreover, the experiments still to be described make two other facts certain. The first is that, when excess of peroxide is employed, the hydrolysing action becomes imperceptible long before the oxidising action is finished, that is, while there is still much cyanide, as well as peroxide, unchanged. The second fact is that the catalytic decomposition of the peroxide does not begin, or at any rate does not cause evolution of oxygen gas, until the cyanide is gone or on the point of vanishing. The whole action may thus be divided into three stages as follows.

First stage: the cyanide undergoes both hydrolysis and oxidation, and therefore disappears faster than the peroxide, no free oxygen appearing.

Second stage: the residual cyanide undergoes oxidation only, and therefore disappears equimolecularly with the peroxide, no free oxygen appearing.

Third stage: the residual peroxide, if any, after disappearance of the cyanide, is catalytically decomposed, and oxygen gas is evolved. This stage does not occur unless the initial ratio of peroxide to cyanide exceeds about 4 : 5.

The evidence on which these statements are based was obtained in the following manner.

Potassium cyanide and hydrogen peroxide solutions were made up of approximately predetermined strength, each in a stoppered 100 c.c. flask, and placed in a thermostat maintained at 20·0°. The exact strength of each solution was determined by titration immediately before mixing, equal volumes being removed for this purpose, and half of each value so found was set down as the initial strength of the mixture. The cyanide was decanted into a larger thin glass flask (also in the thermostat), and the experiment was afterwards begun by rapidly adding the peroxide and starting a stop-watch. Care was taken to drain both flasks always to the same extent, and to ensure complete immediate mixture by rapid rotation of the large flask.

The temperature of the mixture was in some cases observed by means of an immersed thermometer. Generally it showed a rapid rise of a few tenths of a degree above the thermostat temperature, followed by a very slow fall to it. In those cases where action was slower the disturbance was proportionately less, but all the results are undoubtedly affected to some extent by this cause, although the errors due to it cannot be large except in the case of the strongest solutions.

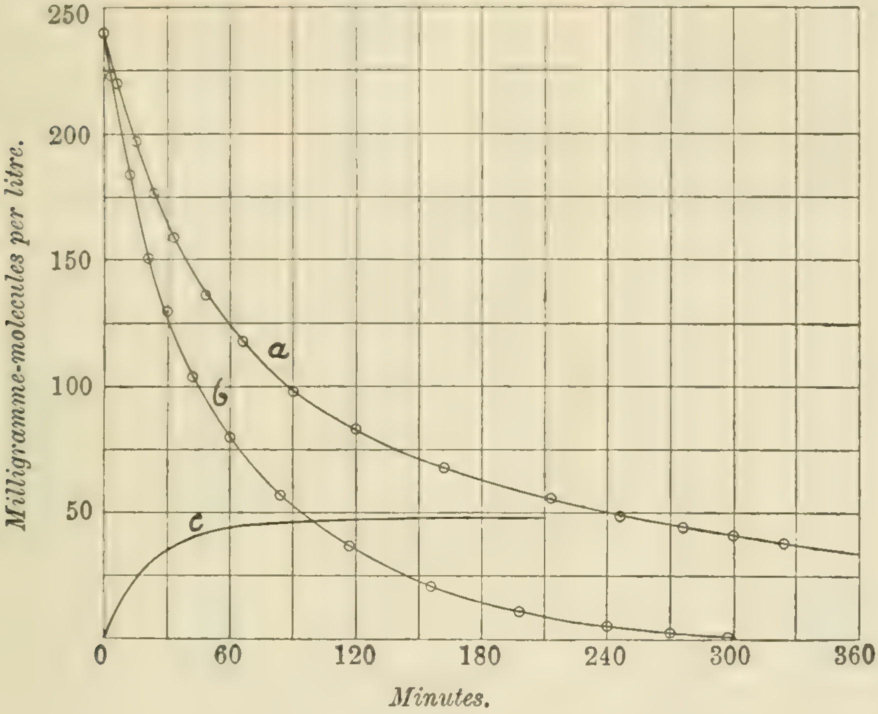
The course of the reaction was followed by withdrawing samples at short intervals and titrating alternately for cyanide and peroxide. Each sample intended for cyanide determination was delivered into a beaker containing some alkaline iodide indicator and then rapidly titrated with $N/40$ silver nitrate, and each sample for peroxide was delivered into excess of dilute sulphuric acid and at once titrated with $N/10$ potassium permanganate. Thus, when 5 c.c. samples were used, each c.c. of the reagent corresponded to one centigram-molecule of potassium cyanide or hydrogen peroxide per litre of the solution. It should be mentioned that the delivery of the test samples into excess of alkali or acid tends in either case greatly to retard further action, as will be shown later. No known systematic error affects the results, which are believed to be trustworthy.

As a rule, a portion of the mixture was removed at the commencement of the experiment to a small flask in the thermostat and put in connexion with a gas burette for the measurement of oxygen evolved. It was found that supersolution occurred, which could be partly counteracted by shaking the flask, but that, even with this precaution, the measurements were not reliable. They served, however, to prove the non-formation of oxygen during the early stages of the action, and to indicate the rapid evolution which sets in practically simultaneously with the disappearance of appreciable cyanide. The same facts are very clearly proved also by observing the liquid sucked up from time to time into the sampling pipette, where the reduced pressure favours the formation of gas bubbles at the earliest opportunity. After the beginning of what has been called the third stage of the action, this bubbling is so brisk that some care is necessary in sampling to take a correct measure of liquid.

After it was no longer possible to detect peroxide, the residual liquid was, as a rule, subjected to quantitative analysis. The results of these determinations have been discussed already and are summarised in Table I. The numbers there used to designate the separate experiments are adhered to in the sequel.

In the following tables, times are given in minutes and all other values in milligram-molecules per litre, and the symbols that head the various columns are defined as follows. A and B stand respectively for the original concentrations of peroxide and cyanide, $A-x$ and $B-y$ representing their residual concentrations at any time (t), as determined by titration. Inasmuch as no oxygen is liberated or otherwise used up until the third and last stage of the action is entered on (namely, until the cyanide has vanished), it is obvious that, until then, x is the measure of the oxidation products (cyanate and carbonate) and $y-x$, which is represented by the symbol w, is that of the hydrolysis product (formate). The maximum value reached by w is expressed as W.

Curves were drawn to represent the results of each experiment, and



EXPT. II.

a. Peroxide curve. *b.* Cyanide curve. *c.* Hydrolysis (by difference).

contemporaneous values were read from them and are given in the tables. The case of Expt. II, which may be taken as typical, is shown in the accompanying figure, in which curves are given for the peroxide and cyanide, and their differences, which are the values of w, since in this case the initial concentrations are equal. Every curve drawn passed through ten or more experimental points, so that the interpolated simultaneous values given in the tables may be taken as trustworthy.

Table IV.—*Expt.* I. $A : B = 0{\cdot}988$.

t.	$A-x$.	$B-y$.	x.	y.	w.
0	477	483	0	0	0
7·5	384	320	93	163	70
15	312	236	165	247	82
22·5	261	173	216	310	94
30	227	134	250	349	99
37·5	203	104	274	379	105
45	185	84	292	399	107
52·5	167	69	310	414	104
60	155	56	322	427	105
75	134	35	343	448	105
90	119	19	358	464	106
105	105	9	372	474	102
120	95	3	382	480	98
150	76	0	—	—	—
180	63	—	—	—	—

Note.—Oxygen evolution perceptible at and after 150 minutes.

$W : B = 105 : 483 = 0{\cdot}217$.

Table V.—*Expt.* II. $A : B = 1{\cdot}00$.

t.	$A-x$.	$B-y$.	x.	y.	w.
0	240	240	0	0	0
7·5	216	202	24	38	14
15	196	171	44	69	25
30	165	130	75	110	35
45	141	100	99	140	41
60	123	80	117	160	43
90	99	53	141	187	46
120	83	36	157	204	47
150	71	23	169	217	48
180	63	14	177	226	49
210	57	9	183	231	48
240	51	5	189	235	46
270	46	2	194	238	44
300	41	0	199	240	41
330	37	—	—	—	—
360	33	—	—	—	—
420	26	—	—	—	—
480	20	—	—	—	—
540	14	—	—	—	—
600	9	—	—	—	—

Note.—Oxygen evolution perceptible at and after 300 minutes.

$W : B = 48 : 240 = 0{\cdot}200$.

Table VI.—*Expt.* III. $A : B = 1{\cdot}02$.

t.	$A-x$.	$B-y$.	x.	y.	w.
0	127	125	0	0	0
7·5	121	115	6	10	4
15	114	104	13	21	8
30	104	90	23	35	12
45	96	80	31	45	14
60	88	70	39	55	16
90	76	55	51	70	19
120	66	44	61	81	20
180	52	29	75	96	21
240	43	20	84	105	21
300	37	14	90	111	21

TABLE VI (continued).—*Expt.* III. $A : B = 1\cdot02$.

t.	$A - x$.	$B - y$.	x.	y.	w.
360	33	9	94	116	22
420	29	5	98	120	22
480	25	2	102	123	21
540	23	1	104	124	20
600	17	0	—	—	—
660	13	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 600 minutes.

$W : B = 21 : 125 = 0\cdot168$.

TABLE VII.—*Expt.* IV. $A : B = 1\cdot20$.

t.	$A - x$.	$B - y$.	x.	y.	w.
0	299	248	0	0	0
7·5	270	202	29	46	17
15	244	164	55	84	29
22·5	220	136	79	112	33
30	205	114	94	134	40
37·5	190	95	109	153	44
45	177	80	122	168	46
60	157	58	142	190	48
75	143	42	156	206	50
90	132	31	167	217	50
105	122	21	177	227	50
120	115	14	184	234	50
135	107	8	192	240	48
150	101	4	198	244	46
180	89	0	—	—	—
240	70	—	—	—	—
300	55	—	—	—	—
360	43	—	—	—	—
420	32	—	—	—	—
480	22	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 180 minutes.

$W : B = 50 : 248 = 0\cdot202$.

TABLE VIII.—*Expt.* V. $A : B = 1\cdot02$.

t.	$A - x$.	$B - y$.	x.	y.	w.
0	254	248	0	0	0
7·5	229	208	25	40	15
15	206	176	48	72	24
30	173	127	81	121	40
45	149	99	105	149	44
60	130	78	124	170	46
75	117	61	137	187	50
90	105	49	149	199	50
120	88	32	166	216	50
150	75	20	179	228	49
180	66	11	188	237	49
210	59	6	195	242	47
240	55	2	199	246	47
270	48	0	—	—	—
300	42	—	—	—	—
360	30	—	—	—	—
420	21	—	—	—	—
480	13	—	—	—	—
540	8	—	—	—	—

NOTE.—Oxygen evolution perceptible after 270 minutes.

$W : B = 50 : 248 = 0\cdot202$.

TABLE IX.—*Expt.* VI. $A : B = 0{\cdot}82$.

t.	$A - x$.	$B - y$.	x.	y.	w.
0	204	249	0	0	0
7·5	184	220	20	29	9
15	167	190	37	59	22
30	138	151	66	98	32
45	116	123	88	126	38
60	101	101	103	148	45
90	80	79	124	170	46
120	63	61	141	188	47
180	45	38	159	211	52
240	34	25	170	224	54
300	25	17	179	232	53
360	20	12	184	237	53
480	13	5	191	244	53

NOTE.—No oxygen gas formed. $W : B = 53 : 249 = 0{\cdot}213$.

TABLE X.—*Expt.* VII. $A : B = 0{\cdot}78$.

t	$A - x$.	$B - y$.	x.	y.	w.
0	196	251	0	0	0
7·5	176	220	20	31	11
15	159	192	37	59	22
30	133	158	63	93	30
45	112	128	84	123	39
60	97	110	99	141	42
90	76	85	120	166	46
120	61	67	135	184	49
180	41	44	155	207	52
240	29	32	167	219	52
300	22	25	174	226	52
360	17	20	179	231	52
420	13	16	183	235	52
480	11	13	185	238	53
540	9	10	187	241	54
720	5	6	191	245	54

NOTE.—No oxygen gas formed. $W : B = 53 : 251 = 0{\cdot}211$.

TABLE XI.—*Expt.* VIII. $A : B = 0{\cdot}60$.

t.	$A - x$.	$B - y$.	x.	y.	w.
0	149	248	0	0	0
7·5	135	227	14	21	7
15	120	204	29	44	15
30	102	176	47	72	25
45	86	155	63	93	30
60	73	140	76	108	32
90	54	119	95	129	34
120	41	102	108	146	38
180	26	84	123	164	41
240	16	72	133	176	43
300	11	66	138	182	44
360	8	61	141	187	46
480	4	57	145	191	46
580	2	55	147	193	46

NOTE.—No oxygen gas formed. $W : B = 46 : 248 = 0{\cdot}185$.

The values of $W : B$ appended to the preceding tables have been collected already in the last column of Table I, where they were compared with the corresponding values deduced from the quantitative determinations of carbonate and cyanate and with the direct determinations of formate. Similar values were also deduced from the measurements of oxygen gas evolved, as indicated in Tables II and III; so that there can be but little doubt of the correctness of the conclusion, which has been based on all these methods of inquiry, that the final hydrolysed fraction ($W : B$) is nearly independent of the initial concentrations (A and B), provided that the ratio of these ($A : B$) is not much below 0·8. The following summary includes a measurement of $W : B$ made with a solution containing at the outset 1 gram-molecule of potassium cyanide and an equivalent amount of hydrogen peroxide per litre. This was useless for testing the velocity of the action, as strong cooling had to be resorted to during the first stage, but it served perfectly for the measurement of W in the second stage.

TABLE XII.—*Hydrolysis Fractions Found by Different Methods.*

Initial KCN in gram-molecules per litre.........	1	0·5	0·25	0·125
Hydrolysis fraction from velocity tests	0·22	0·22	0·20	0·17
,, ,, ,, oxidation products ...	—	0·22	0·21	0·18
,, ,, ,, formate found	—	0·20	0·18	0·16
,, ,, ,, free oxygen found ...	—	0·22 to	0·20	—

The Rate of the Oxidising Action.

Facts already proved make it evident that this rate is given by the slope of the peroxide curve at any moment, so long as there is residual cyanide present. Inspection of the peroxide curve of Expt. II (see figure) shows that it has, until the last stage of the action is setting in, the form characteristic of actions of the second order, or that $\frac{dx}{dt} = k(A-x)^2$. This is also found to hold good in other experiments in which the peroxide and cyanide are originally equimolecular, or when $B = A$, but examination of other cases, where the initial strengths are unequal, shows that the equation must be written $\frac{dx}{dt} = k(A-x)(B-x)$. Expressed in words, this means that the rate of formation of oxidation products (cyanate and carbonate) is proportional at any moment to the concentration of the peroxide and to the sum of the concentrations of the cyanide and its hydrolysis product; for $B-x$ is the same thing as $B-y$ (cyanide) $+w$ (formate). Although the theoretical interpretation of this presents difficulties which have not been overcome by further investigation, it is easy to show that the equation is in agreement with the experimental facts. It may be tested in the first place by calculating the values of k by means of the well-known expression obtained by integrating the above equation for actions of the second order, namely, $kt = \frac{1}{(B-A)}\log_e\frac{A(B-x)}{B(A-x)}$, or, for the special case where $B = A$, as in Expt. II, $kt = \frac{x}{A(A-x)}$. The results of such calculation are shown in Table XIII, where the k values are given for gram-molecules per litre per minute multiplied by 1000. Their approximation to constancy is certainly noteworthy, especially as the figures cover practically the whole range of each oxidation. The divergencies, such as they are, are undoubtedly due in the main to internal heating, as already explained.

TABLE XIII.—*Values of the Velocity Constant* ($k \times 10^3$) *of the Oxidising Action at* 20°.

t.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
7·5	72	62	61	59	61	57	60	55
15	72	62	62	62	66	58	60	55
22·5	77	—	—	67	—	—	—	—
30	77	63	58	65	64	61	60	55
37·5	74	—	—	66	—	—	—	—
45	72	65	60	67	65	63	61	58
60	71	66	59	67	65	63	61	58
75	69	—	—	66	64	—	—	—
90	68	66	60	66	65	61	60	60
105	68	—	—	66	—	—	—	—
120	68	66	62	65	65	63	60	60
150	—	—	—	67	66	—	—	—
180	—	65	65	—	66	61	61	60
210	—	64	—	—	66	—	—	—
240	—	64	66	—	64	60	60	61
300	—	—	66	—	—	61	61	—
360	—	—	65	—	—	60	60	58
420	—	—	66	—	—	—	—	—
480	—	—	70	—	—	60	58	56
540	—	—	70	—	—	—	58	—
720	—	—	—	—	—	—	56	—

NOTE.—For corresponding concentration values, see Tables IV to XI.

In most of the experiments the peroxide curve was traced for a few hours through the final stage, that is, after the disappearance of cyanide and during the escape of oxygen gas. $B - y$ being now nil, the preceding equation becomes $\frac{dx}{dt} = kW(A - x)$, where both k and W are constant, and therefore the curve should appear of the first order. So far as the evidence goes, the action does seem to be unimolecular, but it proceeds somewhat faster than is compatible with the previously determined values of k and W. Similar results were obtained when the finished product was made to act on a fresh supply of peroxide, in which case oxygen evolution proceeded briskly from the first and the course of the last stage of an ordinary experiment was practically repeated.

The Rate of the Hydrolysing Action.

As the destruction of cyanide is due partly to oxidation by the peroxide and partly to hydrolysis under its influence as a catalyst, and as the former action consumes cyanide and peroxide in equimolecular proportion and no oxygen is used in any other way, we have $dy = dx + dw = k(A-x)(B-x)dt + dw$. Now one would naturally expect the hydrolytic action at any moment to be proportional to the concentration of the cyanide and to that of the catalyst, as expressed by the equation $\frac{dw}{dt} = k_1(A-x)(B-y)$, but, if this were the law, w would not cease to increase perceptibly long before the disappearance of either cyanide or peroxide. Further, since this maximum value which it does reach is retained apparently undiminished, as shown both by analysis of the final products and by the curves themselves until incipient oxygen evolution and total destruction of cyanide alter their significance, it follows that no simple theory of consecutive action is tenable, such as that the hydrolysis product is subject to oxidation by the peroxide, nor yet any theory of reversible action. Therefore, in attempting to formulate the facts, we seem driven to represent the cyanide as consisting originally of a larger oxidisable portion and a smaller hydrolysable one, each subject to its own peculiar action and neither convertible into the other. Thus W (the ultimate quantity of hydrolysed product) is the measure of the original hydrolysable portion and $W-w$ is its measure at any later moment, and the rate of hydrolysis under the catalytic influence of the peroxide at any instant is $\frac{dw}{dt} = k_1(A-x)(W-w)$, or, to put it in words, it is proportional to the concentration of the residual peroxide and to the amount of hydrolysis still to be performed. It is easy to show that this leads to a satisfactory calculation of the observed values, although no claim can be made for it as a guide to the true theory of the action.

Starting with the two differential equations already given for oxidation and hydrolysis, namely, $\frac{dx}{dt} = k(A-x)(B-x)$ and $\frac{dw}{dt} = k_1(A-x)(W-w)$, and that obtained by dividing one by the other, namely, $\frac{dw}{dx} = \frac{k_1}{k}\frac{W-w}{B-x}$, and remembering that $x = 0$ and $w = 0$ when $t = 0$, we get the following by integration :

$\frac{A-x}{A} = \frac{A-B}{A-Be^{(B-A)kt}}$, $\frac{B-x}{B} = \frac{(A-B)e^{(B-A)kt}}{A-Be^{(B-A)kt}}$, and $\frac{W-w}{W} = \left(\frac{B-x}{B}\right)^{\frac{k_1}{k}} = \left(\frac{(A-B)e^{(B-A)kt}}{A-Be^{(B-A)kt}}\right)^{\frac{k_1}{k}}$; or, in the special case where $A=B$, $\frac{A-x}{A} = \frac{B-x}{B} = \frac{1}{1+kAt}$ and $\frac{W-w}{W} = \left(\frac{1}{1+kAt}\right)^{\frac{k_1}{k}}$. The evaluation of k from the experimental numbers has been already dealt with. That of k_1 follows; for evidently it is given by

$$\frac{k_1}{k} = \log\frac{W-w}{W}/\log\frac{B-x}{B}.$$

As w is in all cases small, and as it is affected by such titration errors as occur in the determination of either $A-x$ or $B-y$ (and these are as likely to be cumulative as they are to compensate one another), no very precise agreement can be expected between the values of k_1/k so obtained at different points in a curve. But in all the experiments they are never far from the mean value 3·5, and this is found to yield calculated concentrations which agree with those actually recorded within a small limit of error.

In the following tables are given the values of $A-x$ and of w calculated by means of the above equations and those of $B-y$ obtained from the calculated x and w by the rule that $y=x+w$. For each experiment a mean k value has been taken from those given in the appropriate column of Table XIII, and k_1/k has been taken as 3·5. The value of W used is in each case the experimental value already given, which is always near to 1/5 of B. For comparison, the experimental values of $A-x$, w, and $B-y$ are reproduced. In the four experiments selected for tabulation the initial cyanide strength (B) is approximately 0·25 of a gram-molecule per litre, whilst the initial ratio of peroxide to cyanide (A/B) is approximately 1·2, 1·0, 0·8, and 0·6.

TABLE XIV.—*Expt.* IV. *Comparison of Calculated and Found Values.*

	$A-x$.		w.		$B-y$.	
t.	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	299	299	0	0	248	248
7·5	268	270	19	17	198	202
15	242	244	30	29	161	164
22·5	221	220	37	33	133	136
30	204	205	40	40	113	114
37·5	191	190	43	44	97	95
45	178	177	45	46	82	80
60	159	157	47	48	61	58
75	144	143	48	50	45	42
90	132	132	49	50	32	31
120	115	115	49	50	15	14
150	103	101	49	46	3	4

TABLE XV.—*Expt.* V. *Comparison of Calculated and Found Values.*

	$A - x$.		w.		$B - y$.	
t.	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	254	254	0	0	248	248
7·5	227	229	16	15	205	208
15	206	206	24	24	176	176
30	171	173	37	40	128	127
45	148	149	43	44	99	99
60	130	130	45	46	79	78
75	116	117	46	50	64	61
90	105	105	48	50	51	49
120	88	88	48	50	34	32
150	76	75	49	49	21	20
180	67	66	49	49	12	11
210	60	59	49	47	5	6
240	54	55	49	47	0	2

TABLE XVI.—*Expt.* VII. *Comparison of Calculated and Found Values.*

	$A - x$.		w.		$B - y$.	
t.	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	196	196	0	0	251	251
7·5	177	176	13	11	219	220
15	159	159	23	22	191	192
30	133	133	33	30	155	158
45	113	112	39	39	129	128
60	97	97	43	42	109	110
90	76	76	47	46	84	85
120	60	61	49	49	66	67
180	41	41	50	52	46	44
240	30	29	51	52	34	32
360	17	17	51	52	21	20
480	10	10	52	52	13	13

TABLE XVII.—*Expt.* VIII. *Comparison of Calculated and Found Values.*

	$A - x$.		w.		$B - y$.	
t.	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	149	149	0	0	248	248
7·5	134	135	9	7	224	227
15	121	120	16	15	204	204
30	101	102	24	25	176	176
45	86	86	30	30	155	155
60	73	73	34	32	138	140
90	55	54	37	34	117	119
120	43	41	40	38	102	102
180	27	26	42	41	84	84
240	17	16	43	43	74	72
300	12	11	43	44	68	66
360	8	8	44	46	63	61
480	4	4	44	46	59	57

In spite of the close agreement between the found and calculated values, shown in the preceding tables as well as in other cases not cited, the equations on which the calculations are based must, as already stated, be regarded as devoid of direct theoretical significance. If they truly represented the action, we should be forced to conclude, not only that the cyanide consists originally of an oxidisable form and a hydrolysable form in fixed proportion, each behaving independently and inconvertible into the other form, but also that the oxidisable form is subject to simultaneous attack by the peroxide itself and by nascent oxygen liberated through the catalytic agency both of the hydrolysable form and of its hydrolysed product, and that all these three reactions of the peroxide proceed with the same specific velocity. But, apart from its inherent chemical improbability, such a theory is directly contradicted by experiments designed to test the effects of adding at the outset one or more of the products of a previous action. Such initial increase of the hydrolysis product should, according to the equation, have a definite effect on the velocity of oxidation, but the tests show that this is not the case. The only claim, therefore, that is made for the equations given is that they do enable the course of any normal experiment to be foretold with satisfactory accuracy. It seems probable that the agreement is not purely accidental, at all events in the case of the oxidising action, and that it might be explained if methods were available for the detection of intermediate processes while the actions are in progress.

The Influence of the Products on the Oxidation Velocity.

The following experiments were made with the view of testing the apparent truth of the rule that the oxidation proceeds at a rate proportional to the concentration of the peroxide and to the sum of the concentrations of the cyanide and its hydrolysis product.

In the first place, cyanide which had already been treated with peroxide in quantity insufficient to complete the oxidation, although enough almost to finish the hydrolysis, was mixed with a further supply of peroxide so as to continue the oxidation. In this case the differential equation should take the form $\frac{dx}{dt} = k(A-x)(B+C-x)$, where C stands for the constant quantity of original hydrolysed product, and if, for simplicity, A and B be made equal, the integrated equation is $k = \frac{1}{Ct}\log_e\frac{A(A+C-x)}{(A+C)(A-x)}$. The details of the test were as follows. Strong solutions of cyanide and peroxide were mixed in such proportions that the mixture was estimated to contain at the first moment 2541 milligram-molecules per litre of the former and 1521 of the latter. The action was controlled by jacketing with ice and no free oxygen was evolved. Next day, when titration showed no residual peroxide, the strength of the residual cyanide was 405, so that the liquid now contained also 1521 of oxidised and 615 of hydrolysed product. The ratio of the last to the original cyanide was thus rather higher than in the cases previously quoted (0·24 instead of from 0·18 to 0·22), which confirms previous indications that the $W : B$ ratio increases, although not much, as B increases. The solution was now mixed at 20° with an equal volume of peroxide of strength 407, and the course of the action was followed in the usual manner. The initial concentrations were estimated as 202·5 of cyanide, 203·5 of peroxide, and 307·5 of hydrolysed product, so that practically $A = B = 203$. Table XVIII shows the concentrations read from curves drawn through the experimental points and also the values of k calculated by means of the above equation. It is evident that the same law holds here as in normal tests, although k has an unusually small value. The fresh hydrolytic action, although small, is by no means negligible. When the test was repeated, allowing the partially acted-on solution to stand a week before using it, exactly similar results were obtained.

TABLE XVIII.—*Expt.* IX. $C = 308$.

t.	$A - x$.	$B - y$.	w.	k.
0	203	203	0	—
7·5	175	163	12	40
15	151	133	18	41
22·5	129	111	18	42
30	111	92	19	44
37·5	97	77	20	44
45	86	65	21	43
60	66	45	21	44
75	52	31	21	44
90	41	21	20	44
105	34	14	20	43
120	27	9	18	43
150	17	2	15	44
180	9	0	—	—

At the conclusion of Expt. IX, the total formate in the solution was determined by analysis and found to be 315, as compared with the calculated $C + W = 328$, the method yielding, as usual, rather low results.

In the next experiment the initial conditions were different. Whereas in Expt. IX a previously incomplete action, which had never reached the third stage, was finished by adding more peroxide and no fresh cyanide was used, in Expt. X new peroxide and cyanide were mixed with the final products (free from either) of an already completed action. This initial difference proved important, for the oxidation now occurred at a rate proportional to the sum of the concentrations of the cyanide and the *new* hydrolysis product, instead of the *total* hydrolysis exerting its influence, as was to be expected from all earlier results. Indeed, apart from a slight increase in the *W* value, it would be difficult to distinguish this experiment from a normal one. The *k* values given in Table XIX were calculated by the simple bimolecular formula without reference to the added products of the former action.

In order further to test the influence of the addition of the products of hydrolysis, experiments were made in which peroxide was added to cyanide previously mixed with potassium formate, with ammonia, and with formamide. The first showed no recognisable effect, the second produced only a small, general retardation, whilst the third hastened the hydrolytic action (increasing *W*) without influencing the course of the oxidation. In each of these cases, as in the last, the simple bimolecular formula was found to suffice, and the *k* values recorded in the tables were calculated by it.

A comparison of all the evidence, and especially of Expt. IX with the later ones, suggests that that portion of the cyanide which disappears as such, but without oxidation, exists in some intermediate form so long as any unaltered cyanide remains, that in this form it influences the reduction of the peroxide by cyanide in the manner represented in the equation, and that in the last stage, after the total destruction of cyanide, it is converted into formate and ammonia (or possibly formamide) and loses this power. Such a hypothesis, however, presents difficulties of its own, and there is no direct evidence by which it may be tested.

TABLE XIX.—*Expt.* X. *Added Products of Former Action* = 250.

t.	$A-x$.	$B-y$.	w.	k.
0	249	249	0	—
7·5	221	202	19	68
15	198	170	28	69
22·5	180	144	36	68
30	166	124	42	67
45	142	95	47	67
60	125	71	54	66
75	111	52	59	67
90	100	38	62	66
105	90	28	62	68
120	82	20	62	68
150	71	10	61	67
180	62	4	58	67
210	53	0	—	—

NOTE.—Oxygen evolution perceptible at and after 220 minutes.

$W : B = 62 : 249 = 0{\cdot}25$.

TABLE XX.—*Expt.* XI. *Added* $H\cdot CO_2K = 250$.

t.	$A-x$.	$B-y$.	w.	k.
0	251	249	0	—
15	210	174	34	52
30	174	134	38	59
45	150	103	45	60
60	131	81	48	61
75	117	64	51	61
90	106	52	52	60
120	89	35	52	60
150	77	22	53	60
180	68	13	53	60
210	60	7	51	60
240	54	3	49	61
270	48	1	45	62
300	41	0	—	—

NOTE.—Oxygen evolution perceptible at and after 290 minutes.

$W : B = 53 : 249 = 0{\cdot}21$.

TABLE XXI.—*Expt.* XII. *Added* $NH_3 = 250$.

t.	$A-x$.	$B-y$.	w.	k.
0	248	250	0	—
15	208	180	30	52
30	182	143	41	49
45	160	114	48	49
60	143	95	50	49
75	129	81	50	50
90	118	68	52	49
120	99	49	52	51
150	85	36	51	52
180	76	27	51	51
210	69	19	52	50
240	62	13	51	50
270	57	8	51	50
300	52	4	50	51
360	44	0	—	—

NOTE.—Oxygen evolution perceptible at and after 380 minutes.

$W : B = 51 : 250 = 0{\cdot}20$.

TABLE XXII.—*Expt.* XIII. *Added* $HCO\cdot NH_2 = 250$ (*approx*).

t.	$A-x$.	$B-y$.	w.	k.
0	254	254	0	—
15	208	172	36	58
30	172	119	53	63
45	148	89	59	63
60	130	66	64	63
90	106	37	69	61
120	88	19	69	62
150	77	9	68	60
180	69	3	66	59
210	62	1	61	58
240	54	0	—	—

NOTE.—Oxygen evolution perceptible at and after 220 minutes.

$W : B = 68 : 254 = 0{\cdot}27$.

The Effects of Previously Added Alkali and Acid.

As hydrogen peroxide is a weak acid and is known to form salts when added to alkaline solutions, it is reasonable to suppose that the mixture of potassium cyanide and hydrogen peroxide contains hydrogen cyanide (beyond the amount due to normal hydrolysis) and peroxide ions as well as hydrogen peroxide and cyanogen ions and non-ionised salts. It might be suggested that some of these interact to produce cyanate, while others give rise to the hydrolysis product, formate. Although this idea does not point the way to any clear explanation of the observed facts, it seemed desirable to try the effect of previous addition of potassium hydroxide, which should promote ionisation, and of sulphuric acid, which should restrain it. Two experiments were carried out in which the cyanide was mixed beforehand with potassium hydroxide, and two in which the peroxide was mixed beforehand with acid; and Expt. II (see Table V) was done without adding either alkali or acid, but otherwise under identical conditions. The five form a series, as is shown in Table XXIII. The concentrations there are given, as usual, in milligram-molecules per litre, except those of the sulphuric acid, which are in half-molecules. The figures given in the last two columns show the times (in minutes) required for the destruction of half the peroxide and of half the cyanide. In the case of Expt. XVII, which was interrupted, one of these values (given in parentheses) was obtained by extrapolation, but as the curve is practically a straight line there can be no great error. These figures serve to indicate the most striking result of the series of tests, which is that the maximum velocity is attained in the case of pure peroxide and cyanide, the addition of either alkali or acid causing a marked retardation.

TABLE XXIII.

	Initial.		Added.			Time of half action.	
Expt. No.	H_2O_2.	KCN.	KOH.	$\frac{1}{2}H_2SO_4$.	Available alkali.	H_2O_2.	KCN.
XIV	239	239	242	0	481	720	2280
XV........	240	239	120	0	359	136	128
II	240	240	0	0	240	63	34
XVI	240	240	0	120	120	117	45
XVII	239	240	0	242	0	(840)	480

Apart from the general retardation, the effects of the addition of alkali are (1) an evolution of oxygen gas from the start, but quickly diminishing; (2) a decrease of the hydrolytic decomposition of the cyanide as compared with its oxidation. In Expt. XV, with the smaller quantity of alkali, the liberation of oxygen and the hydrolysis roughly balanced one another, and the peroxide and cyanide curves ran close together throughout their course. In Expt. XIV, with the larger quantity, the peroxide curve was at first much steeper than the cyanide curve, the oxygen escape more than balancing the small hydrolysis, but after some hours they became parallel and remained so for a week, no more oxygen escaping and no more hydrolysis occurring. No simple formulæ express the curves in either of these alkaline tests.

The addition of acid appears to increase the hydrolysis in proportion to the oxidation. Apart from this and the general retardation, the whole course of the action with the smaller quantity of added acid (Expt. XVI) is similar to that of the normal test (Expt. II), no oxygen escaping till after the destruction of the cyanide, and the peroxide curve being represented by the usual equation with a diminished k value. But in Expt. XVII, with excess of acid, which was in fact a test of the action of peroxide on hydrogen cyanide, the form of the peroxide curve was quite new, being curiously rectilinear from the start; gas was evolved, and a considerable fraction of the cyanide was oxidised to oxamide (Attfield's action).

These results are shown in the following tables. In the last case the actual readings are given instead of interpolated simultaneous values, so as to show the evidence for the constant velocity of the peroxide decomposition.

TABLE XXIV.—*Expt.* XIV. *Added* KOH = 242.

t.	$A-x$.	$B-y$.	$x-y$.
0	239	239	0
60	207	221	14
150	179	205	26
300	154	191	37
600	127	170	43
1200	101	146	45
2400	71	118	47
3600	52	101	49
5400	34	84	50
7200	24	74	50
9000	17	68	51

NOTE.—Oxygen gas evolved from the start, but with diminishing velocity. Formate found by analysis = 16 = 0·067 B.

TABLE XXV.—*Expt.* XV. *Added* KOH = 120.

t.	$A-x$.	$B-y$.	$x-y$.
0	240	239	0
15	215	203	−11
30	195	183	−11
60	165	154	−10
90	143	135	−7
120	126	123	−2
180	107	107	+1
240	94	96	+3
360	81	84	+4
560	63	66	+4
1260	33	36	+4
2800	7	10	+4
4140	1	4	+4

NOTE.—Oxygen gas evolved during the first four hours with diminishing velocity. Formate found by analysis = 27 = 0·11 B.

TABLE XXVI.—*Expt.* XVI. *Added* $\frac{1}{2}H_2SO_4 = 120$.

t.	$A-x$.	$B-y$.	w.	k.
0	240	240	0	—
7·5	227	211	16	32
15	213	186	27	35
30	191	150	41	36
45	174	120	54	35
60	159	99	60	35
90	136	67	69	35
120	118	45	73	36
150	105	28	77	36
180	95	17	78	35
210	86	9	77	36
240	78	4	74	36
270	71	1	70	37
300	65	0	—	—
360	53	—	—	—
420	43	—	—	—
480	34	—	—	—
540	28	—	—	—
660	16	—	—	—
840	5	—	—	—

NOTE.—Oxygen gas first perceptible between 270 and 300 minutes.

$W : B = 77 : 240 = 0·32$.

TABLE XXVII.—*Expt.* XVII. *Added* $\frac{1}{2}H_2SO_4 = 242$.

t.	$A-x$.	x/t.	t.	$B-y$.
0	239	—	0	240
9	237·5	0·167	4·5	228
24	235	0·167	15	217
51	230·5	0·167	30	212·5
72	228	0·153	60	204·5
102	224	0·147	90	197·5
132	219	0·152	121	191
180	212·5	0·147	174	179
297	196	0·145	291	158
453	174	0·143	447	127
564	157	0·145	558	107·5
672	142	0·144	669	90

NOTE.—Some gas evolved and oxamide crystals formed.

Summary and Conclusions.

1. Hydrogen peroxide and potassium cyanide react exothermically in aqueous solution at the ordinary temperature.

2. The peroxide is reduced without escape of oxygen so long as residual cyanide is present, but any excess of peroxide is afterwards decomposed fairly rapidly into water and oxygen.

3. The products of the oxidation of the cyanide, which do not include oxamide or oxalate, are potassium cyanate and potassium and ammonium carbonates. The ratio of these depends on the amount of peroxide used. Cyanate is the primary product, and tends to be converted by hydrolysis into carbonate through the catalytic agency of the peroxide.

4. A part of the cyanide is converted by hydrolysis, without oxidation, into potassium formate and ammonia. Here also the peroxide acts as catalyst.

5. The total oxidation product (cyanate and carbonate) accounts for about four-fifths of the original cyanide, and the hydrolysis product (formate) for about one-fifth.

6. The peroxide curve, so long as unchanged cyanide remains, is of the second order and accords well with the equation

$$\frac{dx}{dt}=k(A-x)(B-x),$$

where A is the initial concentration of the peroxide, B is that of the cyanide, and x is the measure of the peroxide reduced, or cyanide oxidised, at time t. $B-x$ is the sum of the residual cyanide $(B-y)$ and its hydrolysed product (w).

7. The hydrolysed product (w) reaches its maximum and final value $(W=0{\cdot}2\ B$, nearly) before the completion of the oxidising action, and thereafter the slopes of the peroxide and cyanide curves are equal. The rate of hydrolysis is expressed by the empirical rule that $\frac{dw}{dt}=k_1(A-x)(W-w)$.

8. If the solutions are made to contain at the outset the ultimate products of the action itself, as well as fresh cyanide and peroxide, these products do not exert the influence indicated by the above equations. Hence, some unknown intermediate condition probably occurs while the action is in progress.

9. The addition of free alkali (KOH) at the outset greatly retards the whole action, diminishes the hydrolysis relatively to the oxidation, and causes the escape of oxygen gas in the early stages. The addition of ammonia has very little effect.

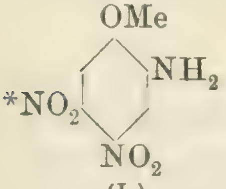
10. The addition of free acid (H_2SO_4) at the outset also greatly retards the whole action, and appears to increase the hydrolysis. If enough acid be added to convert all the potassium cyanide into hydrogen cyanide, oxamide crystals are slowly formed (Attfield's action) and the peroxide curve becomes rectilinear.

UNIVERSITY OF MELBOURNE.

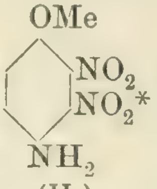
CXXXIX.—*The Diazotisation of Dinitroanisidines and Related Compounds.*

By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY.

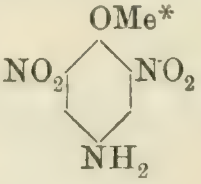
IN the last paper dealing with this series of researches (Trans., 1906, **89**, 923) the conclusion was reached that when a nitro-group is in the ortho- or para-position with respect to an amino-group no displacement of the nitro-group takes place on diazotisation unless there is a second nitro-group adjacent to the first (mobile) group. The only two known dinitroanisidines in which this condition is fulfilled are those derived respectively from ortho- and para-anisidine (I and II), which have been dealt with in previous communications. The dinitro-*p*-anisidine (III: Meldola and Stephens, Trans., 1905, **87**, 1204), the dinitro-*m*-anisidine (IV: Meldola and Stephens, Trans., 1906, **89**, 927), and the new dinitro-*p*-anisidine recently obtained by Reverdin and Bucky (*Arch. Sci. phys. nat.*, 1906, **22**, 140) do not contain the substituents in the necessary positions:



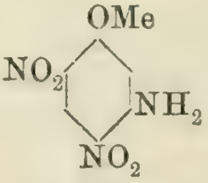
(I.)



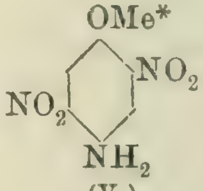
(II.)



(III.)



(IV.)



(V.)

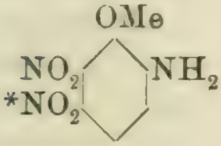
In accordance with this conclusion, the nitro-group marked * in I and II has been found to be displaceable when the compounds are diazotised, whereas no displacement in III, IV, or V takes place under these conditions. On the other hand, it has been found that when a methoxy-group is in the para-position with respect to the amino-group and at the same time has a nitro-group in an adjacent position, demethylation takes place on diazotisation (Meldola and Stephens, Trans., 1905, **87**, 1205). As the final product of demethylation is a diazo-oxide, it appears certain that the elimination of the alkyl radicle must also follow the ortho-para rule. This conclusion is confirmed by the following observations:

(*a*) Compound No. IV complies with only one of the conditions. There is a nitro-group adjacent to the methoxy-group, but the amino-group is in the meta-position. This compound on diazotisation loses neither methyl nor NO_2 (Meldola and Stephens, Trans., 1906, **89**, 928).

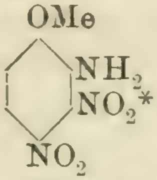
(*b*) Compound No. V complies with both conditions. There is a nitro-group adjacent to the methoxy-group and an amino-group in the para-position. On diazotisation, the diazonium salt yields 2 : 5-dinitrophenol when boiled with alcohol, so that in this case demethylation takes place (Reverdin and Bucky, *Ber.*, 1906, **39**, 2691).

The displaceable methyl groups in III and IV are indicated by the *. In these compounds, the nitro-group in the ortho-position with respect to the methoxy-group is no doubt the determining cause of the mobility of the methyl or methoxy-group.†

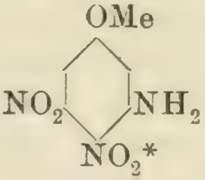
Among the possible dinitroanisidines indicated by theory, there are four other isomerides (VI to IX) in which the configuration is favourable for the displacement of the nitro-group :



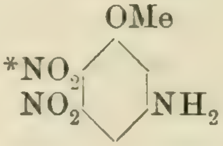
(VI.)



(VII.)



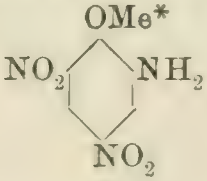
(VIII.)



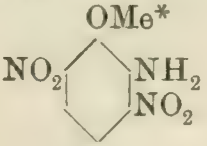
(IX.)

None of these compounds is, however, at present known, and as the nitro-groups marked * might be expected to be displaceable, an attempt will be made to prepare some of them in order to test the generality of the conclusions reached at this stage of the investigations. Compound No. VI is of special interest owing to the circumstance that both the nitro- and methoxy-groups are in positions favourable for displacement.

Compounds No. X (the methyl ether of picramic acid) and No. XI (unknown) contain the substituents in positions favourable for the displacement of the methyl (methoxy) group :



(X.)



(XI.)

The conclusions arrived at concerning the conditions which determine the displacement of nitro- and methoxy-groups on diazotisation are in harmony with the results obtained by other investigators who have been studying the displacement of halogens under similar conditions. This kind of displacement, which has long been known to those who have worked in the field of diazo-chemistry, has been utilised for technical purposes (Badische Co., Fr. Pat. No. 315932 of 1902) and has recently been made the subject of systematic researches by K. J. P. Orton, who has approached the question from the point of view of isomeric change. A consideration of the constitution of the compounds in which this displacement of halogen occurs brings out clearly the same principle—that the displaceable halogen atom must be in the ortho- or para-position with respect to the diazonium group and that the mobility of the halogen, although in this case not absolutely dependent upon, is largely augmented by the proximity of another substituent (halogen atom or nitro-group) in the ortho-position with respect to the displaceable atom. This is most clearly seen on reference to the list of compounds given by Orton (Trans., 1903, **83**, 800) in which the mobility of the halogen atom has been determined by the percentage of free halogen liberated in a given time.

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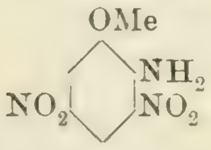
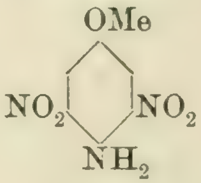
† Whether the process is simply one of demethylation or whether the methoxy-group is eliminated as a whole must for the present remain an open question. On the hypothesis of "isomeric change" it might be expected that it is the methoxy-group which is mobile.

In continuation of our previous work, several attempts have been made to prepare the dinitroanisidine, No. X, corresponding to picramic acid, but hitherto without success. Experiments having for their object the methylation of the silver and potassium salts of acetyl picramic acid invariably resulted in the production of the original compound. Although this dinitroanisidine figures in chemical literature (Beilstein, Vol. II., p. 733), it is doubtful whether it has ever been obtained, as the reduction of trinitroanisole by ammonium sulphide apparently gives rise to other products. The experiments in this direction are, however, not yet completed, and the conclusions will be withheld for a future communication.

In the present paper, the results of diazotising two other dinitroanisidines are made known. Of these, No. XII was first prepared by Blanksma (*Proc. K. Akad. Wetensch. Amsterdam,* 1903, **5**, 650) and No. XIII was described in a former communication by one of the authors and F. G. C. Stephens (Trans., 1905, **87**, 1206):



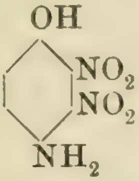
(XII.)

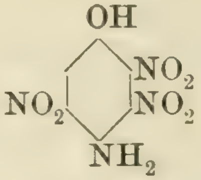


(XIII.)

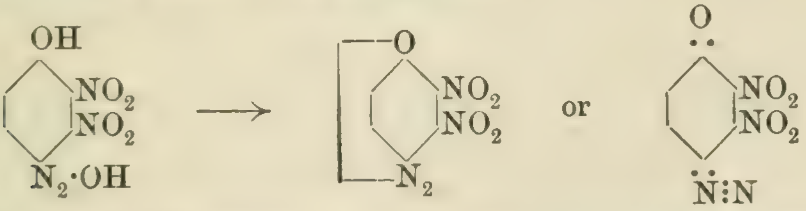
As will be seen on reference to the formulæ, there is no group in either of these compounds in a position favourable for displacement, and, as might have been anticipated, they behave quite normally on diazotisation.

Incidentally in the course of the present investigation we have discovered the hitherto unknown 2 : 3-dinitro-4-aminophenol and we have also succeeded in isolating the 2 : 3 : 5-trinitro-4-aminophenol of which the acetyl derivative was described recently by one of us (Trans., 1906, **89**, 1935). The constitution of these compounds is shown below:





The discovery of these compounds has enabled us to study their products of diazotisation, a point of considerable importance in view of the fact that one of them corresponds to the dinitro-*p*-anisidine investigated from this point of view five years ago (Meldola and Eyre, Trans., 1902, **81**, 988). There has thus been made possible a comparative study of a dinitroaminophenol with its methyl ether, and the special influence of the methoxy-group has by this means been determined. As will be seen from the experimental part, the methoxy-group has a decided "loosening" influence upon the nitro-group, since, under the same conditions of diazotisation as those which cause the displacement of the 3-nitro-group in dinitro-*p*-anisidine (Trans., 1902, **81**, 998), a dinitro-derivative is obtained from the new dinitroaminophenol. This result is no doubt due to the facility with which the diazo-derivative can pass into the comparatively stable para-diazo-oxide (quinonediazide) in the dinitroaminophenol:



In the case of the corresponding dinitroanisidine the quinonediazide must belong to the ortho-series and can only be formed by the elimination of the nitro-group. The trinitroanisidine corresponding to the new trinitroaminophenol has not yet been obtained, and all attempts to prepare it have hitherto failed.

EXPERIMENTAL.

Diazotisation of 3 : 5-*Dinitro*-o-*anisidine* (3 : 5-*Dinitro*-2-*aminoanisole*).

This dinitroanisidine was prepared from 1 : 3 : 5-trinitrobenzene by the method described by Blanksma (*loc. cit.*). After repeated crystallisation from glacial acetic acid, the compound consisted of rubycoloured needles with a green, metallic lustre melting at 181° (174°: Blanksma):

0·1323 gave 23·05 c.c. moist nitrogen at 18° and 758·5 mm. N = 20·07.

$C_7H_7O_5N_3$ requires N = 19·76 per cent.

This dinitroanisidine dissolves readily in boiling glacial acetic acid with an orange colour, but, on cooling, practically the whole of the substance separates out in a crystalline form. It was not found possible to diazotise the base in acetic acid, but it diazotises readily in sulphuric acid, and the diazonium salt thus formed retains both nitro-groups. This was proved by combining the diazotised base with β-naphthol in alkaline solution and also by replacing the diazonium group by iodine.

On mixing the solution of the diazonium sulphate with an alkaline solution of β-naphthol in the usual way, the azo-compound separates out as a red precipitate. It can be purified by crystallisation from boiling aniline or acetic anhydride and is then obtained in dark scales with a metallic lustre, melting with decomposition at 291°. It dissolves in strong sulphuric acid with a deep violet colour, becoming red on dilution:

0·1039 gave 13·7 c.c. moist nitrogen at 14·5° and 747 mm. N = 15·07.

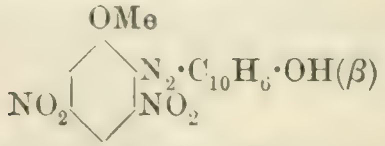
$C_{17}H_{12}O_6N_4$ requires N = 15·25 per cent.

The replacement of the amino-group in this dinitroanisidine by iodine was effected by boiling the diazonium sulphate with hydriodic acid as long as nitrogen was evolved. The product after crystallisation from alcohol was obtained in large, flat, ochreous needles with serrated edges melting at 141·5°. Analysis proved it to be iododinitroanisole:

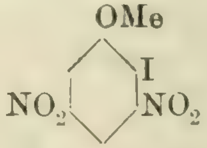
0·1619 gave 11·85 c.c. moist nitrogen at 14° and 749 mm. N = 8·49.
0·1139 ,, 0·0828 AgI. I = 39·3.
0·3022 by Berry's method * required 9·35 c.c. $N/10\,AgNO_3$ = 0·1186 of iodine; I = 39·25.

$C_7H_5O_5N_2I$ requires N = 8·66; I = 39·18 per cent.

The constitution of these compounds is shown by the formulæ:



(M. p. 291° with decomposition.)



(M. p. 141·5°.)

Diazotisation of 3 : 5-*Dinitro*-p-*anisidine* (3 : 5-*Dinitro*-4-*aminoanisole*).

This dinitroanisidine has already been described in a former paper (Trans., 1905, **87**, 1206). As the preparation of this compound in quantity has presented considerable difficulties, we give further details respecting the method which, after much experimenting, we have found most advantageous. Following the instructions given by Reverdin, who discovered the dinitroaminophenol corresponding to this dinitroanisidine, we prepared in the first place dibenzoyl-*p*-aminophenol and then, by nitration, obtained from this the dinitrobenzoyl derivative of the dinitroaminophenol. The nitration of the dibenzoyl-*p*-aminophenol was carried out by dissolving the substance in a mixture of equal volumes of concentrated sulphuric and fuming nitric acids cooled in ice, 10 grams of the dibenzoyl compound requiring about 130 c.c. of the mixture of acids. After the addition of the whole of the substance, the solution was removed from the ice-bath and the temperature allowed to rise to that of the atmosphere, at which temperature it was allowed to stand for about two hours and then finally heated on the water-bath for about an hour. The solution was then poured on to ice and the product collected, washed free from acid, and crystallised from alcohol or acetic acid. At this stage, the dinitrodibenzoyl-3 : 5-dinitro-*p*-aminophenol of Reverdin was obtained, and from this certain new derivatives have been prepared which are most conveniently described here.

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* See *Chem. News*, 1906, **94**, 188.

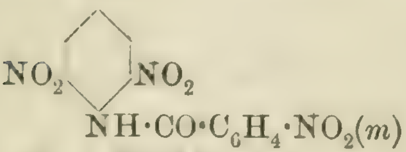
The tetranitro-compound is easily hydrolysed by the action of a cold alcoholic solution of sodium hydroxide, the *O*-nitrobenzoyl group being removed. The product after crystallisation from alcohol consists of white, silky needles, soluble in aqueous alkali with an orange colour and having a melting point of 215·5° :

0·0596 gave 8·1 c.c. moist nitrogen at 9·5° and 757·3 mm. N = 16·25.
$C_{13}H_8O_8N_4$ requires N = 16·13 per cent.

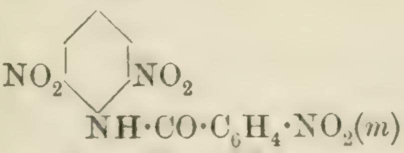
On hydrolysis by sulphuric acid and purification of the product by crystallisation from water, Reverdin's dinitro-*p*-aminophenol was obtained in red needles melting at 240·5° (corrected by reference to short-stemmed standard thermometer). The compound was methylated by dimethyl sulphate in presence of alkali and, after crystallisation from acetic acid, consisted of white, prismatic needles melting at 174—175° :

0·1212 gave 15·2 c.c. moist nitrogen at 11·5° and 771·2 mm. N = 15·14.
$C_{14}H_{10}O_8N_4$ requires N = 15·46 per cent.

The constitution of these compounds is shown by the formulæ :



(M. p. 215·5°.)



(M. p. 174—175°.)

All attempts to hydrolyse the above methyl derivative were unsuccessful. The compound is decomposed completely by alkaline hydrolysing agents, and sulphuric acid fails to remove the nitrobenzoyl group at moderate temperatures, or at higher temperatures removes both this and the methyl group. The compound had therefore to be abandoned as a source of the required dinitro-*p*-anisidine. The latter was ultimately obtained in quantity by starting from Reverdin's 3 : 5-dinitro-*p*-aminophenol, which we have found to be most conveniently prepared by hydrolysing the dinitrodibenzoyl derivative prepared as above by means of sulphuric acid, and purifying the product, as recommended by its discoverer, by crystallisation from hot water in order to free it from *m*-nitrobenzoic acid. The dinitroaminophenol is then acetylated by heating for a short time with acetic anhydride so as to convert it into the *N*-monoacetyl derivative (m. p. 182°: Reverdin, *Arch. Sci. phys. nat.*, 1904, **18**, 439), and the latter methylated by methyl iodide and silver oxide and hydrolysed by sulphuric acid as described in the former paper (*loc. cit.* p. 1206).

3 : 5-Dinitro-*p*-anisidine could not be diazotised in acetic acid solution. It diazotises readily in sulphuric acid, and the diazonium sulphate solution on being mixed with an alkaline solution of β-naphthol gives a non-phenolic azo-compound which, after crystallisation from glacial acetic acid, consisted of large needles of a ruby-red colour by transmitted light and having a green, metallic lustre. The melting point is 226°, and the compound dissolves in alcoholic soda with a dull red colour, in boiling acetic acid with an orange colour, and in strong sulphuric acid with a deep violet colour becoming red on dilution. Analysis showed that two nitro-groups are contained in the molecule:

0·1286 gave 16·25 c.c. moist nitrogen at 16° and 766·6 mm. N = 14·86.

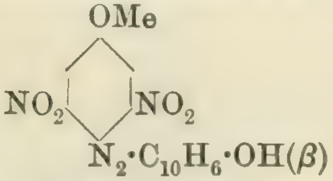
$C_{17}H_{12}O_6N_4$ requires N = 15·25 per cent.

A further quantity of the diazonium sulphate was decomposed by boiling with hydriodic acid as long as nitrogen was evolved. The product was purified by repeated crystallisation from acetic acid and alcohol alternately, and finally obtained in dense, ochreous prisms melting at 161—162°. Analysis proved the compound to be iododinitroanisole:

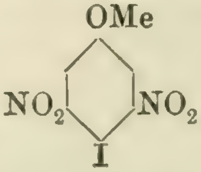
0·0970 gave 7·15 c.c. moist nitrogen at 15·5° and 765·1 mm. N = 8·67.

$C_7H_5O_5N_2I$ requires N = 8·66 per cent.

The constitutional formulæ of these compounds are given below:



(M. p. 226°.)



(M. p. 161—162°.)

2 : 3-*Dinitro*-4-*aminophenol and its Products of Diazotisation under Various Conditions.*

This compound was discovered incidentally in the course of experiments having for their object the study of the influence of the *O*-acetyl group in determining the position of entry of nitro-groups in acetylated *p*-aminophenol. It had long been known that diacetyl-*p*-aminophenol on nitration gives the diacetyl derivative of 3-nitro-*p*-aminophenol (Hähle, *J. pr. Chem.* 1901, [ii], **63**, 63), and this by partial hydrolysis yields 3-nitro-4-acetylaminophenol (Reverdin and Dresel, *Arch. Sci. phys. nat.*, 1904, **18**, 442). In this last compound the hydroxyl group is therefore unprotected by acetyl, and it became of interest to ascertain whether by further nitration a dinitrophenol could be obtained corresponding to one of the known dinitroanisidines. Under all conditions with fuming nitric acid, either alone or in acetic acid solution, the nitroacetylaminophenol * is converted into 2 : 3 : 5-trinitro-4-acetylaminophenol. By using a weaker acid, however (1·42 sp. gr.), and dissolving the mononitro-compound in this acid cooled in ice, the nitration can be regulated so as to give a dinitroacetylaminophenol. The best result is obtained by dissolving 5 grams of the mononitro-compound in about 35 c.c. of the cooled acid and, after standing for an hour, pouring the solution on to ice. The product, after being collected and washed, can be purified by crystallisation from hot water or dilute acetic acid. It consists of large, yellow needles melting at 199·5° with decomposition and beginning to darken about 8° below this temperature.

0·1389 gave 20·85 c.c. moist nitrogen at 19° and 770·5 mm. N = 17·49.
0·1141 „ 16·4 „ „ „ „ 10° „ 765·3 mm. N = 17·33.
$C_8H_7O_6N_3$ requires N = 17·47 per cent.

The dinitroacetylaminophenol thus obtained was shown to have the nitro-groups in positions 2 : 3 by methylating the compound in methyl alcohol by silver oxide and methyl iodide. There was obtained by this method the 2 : 3-dinitro-*p*-acetanisidide of m. p. 230—231°, giving the 2 : 3-dinitro-*p*-anisidine of m. p. 188° (Meldola and Eyre, Trans., 1902, **81**, 990). The constitution of the compound having been established by this result, it appeared probable that the 3-nitro-group would be found to be displaceable, as the configuration is favourable for a "mobility" of this group. Some of the compound was accordingly dissolved in aniline and the solution kept warm on the water-bath for three to four hours. The excess of aniline having been removed by dilute hydrochloric acid, the product was dissolved in dilute sodium hydroxide, the solution filtered to remove aminoazobenzene, and the phenolic portion precipitated by acid. To ensure complete conversion into an iminazole, the product, after being collected, washed, and dried, was heated for a short time on the water-bath with concentrated sulphuric acid and then recovered by diluting the solution with water and neutralising the acid by sodium hydroxide. The product after crystallisation from dilute alcohol was obtained as an ochreous, microcrystalline powder melting at 200—203·5°:

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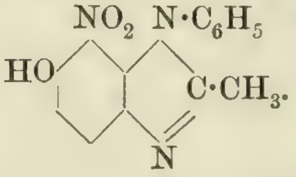
* The hydrolysis is most conveniently carried out by suspending the diacetyl compound in cold water and adding sodium hydroxide solution, with constant agitation, until the substance passes into solution. In the course of a few minutes, the hydrolysis is complete and the monoacetyl derivative is precipitated by acidifying the solution with hydrochloric acid.

0·1375 gave 18·7 c.c. moist nitrogen at 18° and 760 mm. N = 15·7.

$C_{14}H_{11}O_3N_3$ requires N = 15·65 per cent.

The compound is phenolic and has all the properties of an iminazole. The 3-nitro-group of the new dinitroacetylaminophenol is thus shown to be mobile, and from its mode of formation the iminazole must be:



(7-Nitro-6-hydroxy-1-phenyl-2-methylbenziminazole.)

The dinitroacetylaminophenol cannot be hydrolysed by alkalis, as it is readily decomposed under these conditions. It can be readily hydrolysed by heating on a water-bath for a few minutes with concentrated sulphuric acid, but the dinitroaminophenol is also very unstable, and the course of the hydrolysis must be followed by frequent tests or the whole of the product may be lost by decomposition. The best method is to heat the sulphuric acid solution of the monoacetyl compound in a flask on the water-bath until a drop withdrawn and diluted with water on a watch-glass gives a bright red, crystalline deposit which does not increase in intensity of colour after successive tests. The whole operation is complete in a few minutes, and must be at once arrested when the requisite stage has been reached by rapidly cooling the flask in water or melting ice. On pouring the acid solution on to ice, the dinitro-compound is precipitated as a red, crystalline deposit which can be collected on a filter and washed free from acid, as it is so feebly basic that its salts are completely dissociated by water. It has not been found possible to isolate the dinitroaminophenol in a state suitable for analysis, since it begins to decompose with the evolution of gas as soon as it is freed from acid by washing on the filter. The mobile nitro-group in proximity to the amino-group is no doubt the determining cause of the instability.

Diazotisation in Presence of Sulphuric Acid.—Some of the dinitroaminophenol, prepared as above, was dissolved in glacial acetic acid, some concentrated sulphuric acid added to the solution, and then diazotisation effected in the usual way. A diazo-oxide (quinonediazide) is apparently formed at this stage, as the solution on dilution with water gives a yellow precipitate. As our main object was to ascertain whether the 3-nitro-group was eliminated, the diazotised product was at once decomposed by boiling with hydriodic acid in the usual way, and the compound thus obtained, after purification and repeated crystallisation from dilute alcohol, consisted of ochreous scales melting at 140° and proving on analysis to be iododinitrophenol:

0·1185 gave 8·8 c.c. moist nitrogen at 13° and 770·1 mm. N = 8·89.

$C_6H_3O_5N_2I$ requires N = 9·05 per cent.

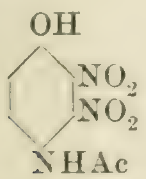
The above result having shown that no elimination of the nitro-group takes place, the experiment was repeated with the substitution of cuprous chloride for hydriodic acid. In this case, no attempt was made to isolate the dinitroaminophenol, but the sulphuric acid solution, after the hydrolysis of the acetyl compound, was diluted with water and diazotised with sodium nitrite. The solution was then mixed with a solution of cuprous chloride and heated until the decomposition was complete. The product was volatile to a small extent in steam, but the main portion separated from the cold solution in a crystalline form. After being freed from copper compounds by alkaline extraction, filtration, and precipitation by acid, the compound was purified by crystallisation from alcohol and obtained in transparent, colourless prisms melting at 127° and proving on analysis to be chlorodinitrophenol:

0·0993 gave 11·3 c.c. moist nitrogen at 18° and 755·6 mm. N = 13·06.
0·1473 „ 0·0954 AgCl. Cl = 16·01.

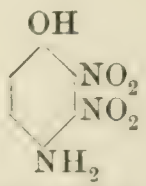
$C_6H_3O_5N_2Cl$ requires N = 12·85; Cl = 16·22 per cent.

The compound is phenolic in character, soluble in all the ordinary solvents and in boiling water; it is slightly volatile in a current of steam, and by this means is obtained in slender, white needles.

The constitution of the foregoing compounds is shown by the formulæ:



(M. p. 199·5°.)



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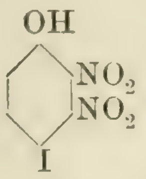
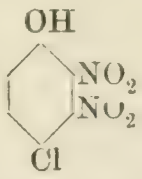
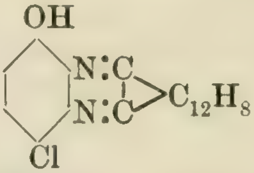


(M. p. 140°.)



(M. p. 127°.)

Confirmation of the ortho-position of the nitro-groups was obtained by reducing some of the chlorodinitrophenol by zinc dust in acetic acid solution and heating with phenanthrenequinone in the same solvent, so as to bring about azine condensation. A phenolic azine containing chlorine was thus obtained which, after crystallisation from dilute alcohol, consisted of small, orange needles melting at 131° and having the composition of the azine:



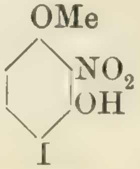
0·0109 gave 0·75 c.c. moist nitrogen at 16·5° and 772·4 mm. N = 8·14.
$C_{20}H_{11}ON_2Cl$ requires N = 8·49 per cent.

It is thus shown that when diazotised in presence of a strong acid the dinitroaminophenol behaves like the corresponding dinitroanisidine.

Diazotisation in Presence of Acetic Acid.—Some of the dinitroaminophenol was prepared as above, freed as rapidly as possible from sulphuric acid by washing with water, and dissolved in glacial acetic acid with the addition of sodium acetate to ensure the absence of free mineral acid, the base being then diazotised in the acetic acid solution. On decomposing the product by heating with hydriodic acid, there was obtained the same iododinitrophenol (m. p. 140°) as that resulting from the diazotisation in presence of sulphuric acid:

0·0694 gave 5·4 c.c. moist nitrogen at 20° and 768·3 mm. N = 8·99.
$C_6H_3O_5N_2I$ requires N = 9·05 per cent.

The "loosening" influence of the methyl group is thus brought out very clearly, since the corresponding dinitroanisidine under similar conditions loses the 3-nitro-group. In order to make the comparison more rigid, some 2 : 3-dinitro-*p*-anisidine was diazotised in acetic acid by the method previously described (Trans., 1902, **81**, 998) and the product decomposed by boiling with hydriodic acid. A compound was thus obtained which was crystallised from water and, finally, from dilute acetic acid, and then consisted of minute, ochreous needles melting at 87° and having the composition of the expected iodonitroresorcinol methyl ether:



0·1004 gave 4·1 c.c. moist nitrogen at 19° and 760 mm. N = 4·69.
$C_7H_6O_4NI$ requires N = 4·76 per cent.

(There is simultaneously formed in this reaction a small quantity of a red, crystalline, phenolic substance, which volatilises with the steam and condenses on the watch-glass covering the neck of the flask. The melting point is 143·5°. Very little of this compound was obtained, but an attempt will be made to prepare it in larger quantity.)

The action of cuprous chloride on the product obtained by diazotisation in the absence of mineral acid is remarkable, and will be made the subject of further investigation in connexion with the general question of the action of cuprous chloride on these products of diazotisation (see Trans., 1902, **81**, 997). We may state, as a preliminary result, that the chief product is the 4-chloro-2-nitrophenol of m.p. 87° (Faust and Saame, *Ann. Suppl.*, 1871, **7**, 190), so that the cuprous chloride acts simultaneously as a chlorinating and reducing agent, the 3-nitro-group being removed without replacement by hydroxyl or chlorine. There is also formed in this process a substance crystallising in red needles with serrated edges melting at 120° and giving a benzoyl derivative melting at 94° and crystallising in white needles. The products of diazotisation of 2 : 3 : 5-trinitro-4-aminophenol have also been studied in a preliminary way, and the results will be made known when more fully worked out.

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CXL.—*Permanganic Acid.*

By Matthew Moncrieff Pattison Muir.

In 1830, Hünefeld (*Schweigger's Jahrbuch der Chem. u. Pharm.*, **30**, 133) thought he had obtained manganic acid by adding phosphoric acid to barium manganate, filtering, and evaporating. Hünefeld gave no analyses or proof that he was dealing with a homogeneous substance. In 1832, Mitscherlich (*Pogg. Annalen*, **25**, 287) added an equivalent quantity of sulphuric acid to barium permanganate, and obtained an aqueous solution of permanganic acid, which decomposed, he said, at 30° to 40°. Neither analyses nor direct proofs of the presence of permanganic acid in the solution examined by him were given by Mitscherlich. In 1856, P. Thenard (*Compt. rend.*, **42**, 382) briefly described the preparation of anhydrous permanganic acid, but gave no analytical data. Aschoff, in 1860, described the preparation, and gave proofs of the composition of permanganic anhydride, Mn_2O_7 (*J. pr. Chem.*, **81**, 29). What Terreil, in 1862, took to be permanganic acid—he gave no analyses—was probably the anhydride (*Bull. Soc. chim.*, **4**, 40; translation in *Chem. News*, **6**, 57). In 1870, Speis (*J. pr. Chem.*, [ii], **1**, 421), by adding sulphuric acid to potassium permanganate, obtained a brown deposit, which, he said, was probably manganese sesquioxide mixed with manganous oxide. Kolbe, the editor of the Journal, added a note to say that the brown solid was probably permanganic acid. In 1892, Loven (*Ber.*, **25**, *Ref.* 620), by dissolving permanganic anhydride in water, obtained a 20 per cent. solution of permanganic acid, and showed, by measurements of the electric conductivities of the solution, that permanganic acid is a strong, monobasic acid, comparable with hydrochloric, nitric, chloric, and perchloric acids.

All observers are agreed that a moderately concentrated aqueous solution of permanganic acid readily gives up oxygen to oxidisable substances.

Preparation of Permanganic Acid.—A weighed quantity of barium permanganate, dried at 100°, was dissolved in water; the brown, insoluble residue was dried at 100° and weighed. The specimen of barium permanganate used by me contained 7·8 per cent. of solid matter insoluble in water. Assuming that the difference between the weight of substance treated with water and the weight of insoluble matter was the weight of pure barium permanganate in solution, the equivalent quantity of sulphuric acid in dilute solution was added; after a few days the liquid was filtered through glass wool to free it from precipitated barium sulphate, and the filtrate was concentrated by evaporation in a vacuum over sulphuric acid. Qualitative tests proved the absence of barium and of sulphuric acid from this liquid. The solution had exactly the same appearance as an aqueous solution of potassium permanganate containing about 0·4 per cent. of that salt.

I found that this method gave better results than were obtained by mixing equivalent quantities of silver permanganate and hydrochloric acid in aqueous solution, filtering from silver chloride, and evaporating in a vacuum.

The ratio of the quantities of manganese and oxygen in the liquid was determined by the method described by Thorpe and Hambly in their paper "On Manganese Trioxide" (Trans., 1888, **53**, 175, 182), namely, titration with a standardised solution of ammonium oxalate, re-oxidation by red lead and nitric acid, and re-determination of permanganate by ammonium oxalate. I give some of the results obtained.

	Number of c.c. of ammonium oxalate solution used.	
Volume of liquid used.	Before re-oxidation.	After re-oxidation.
10 c.c.	7·0 c.c.	7·1 c.c.
10 ,,	18·7 ,,	18·5 ,,
10 ,,	18·2 ,,	18·1 ,,
10 ,,	17·4 ,,	17·3 ,,
10 ,,	17·4 ,,	17·2 ,,

The ratios of manganese and oxygen found in solutions prepared at different times, and of different concentrations, are presented in the following table ($Mn = 55$; $O = 16$):

Calculated for Mn_2O_7; $Mn = 49.55$ per cent.; $O = 50.45$ per cent.

Ratio of Mn : O, sum of these two taken as 100.

Manganese.	Oxygen.	Manganese.	Oxygen.
49·80	50·19	49·45	50·55
49·62	50·38	49·65	50·55
49·36	50·64	49·60	50·50

A very small quantity of an aqueous solution of permanganic acid, containing about 10 per cent. of the acid, was allowed to evaporate in the air on a watch-glass. After a couple of days, many very fine, crystalline needles of a violet-blue colour were visible under the microscope, mixed with a network of black solid, on a background of reddish-brown solid matter. After a few more days, the quantity of the brown substance had increased, the crystals had become darker in colour and more opaque, and the black network had spread more continuously throughout the mass. After three or four days, the crystals had broken up into detached black spots, and none of the solid matter was soluble in water. As long as any violet-blue crystals were to be seen under the microscope, water at once dissolved some of the solid and became coloured like a dilute solution of potassium permanganate.

I could only obtain the violet-blue crystals mixed with very considerable quantities of black and brown solid substances. By allowing small weighed quantities of concentrated solutions of permanganic acid to evaporate on watch-glasses until pasty, weighing again, dissolving in water, weighing the insoluble substance, and estimating the acid in solution, I found that the quantity of permanganic acid in the pasty substance varied from 30 to 44 per cent.

It will be shown that the black solid which is produced by the decomposition of concentrated solutions of permanganic acid is almost pure manganese dioxide, and the brown solid which is formed when less concentrated solutions of the acid decompose at the ordinary temperature is MnO,O_x, where x is approximately equal to two-thirds.

I conclude from these observations that permanganic acid, $HMnO_4$, can be obtained in fine, violet-blue, crystalline needles, but not unmixed with oxides of manganese.

In order to obtain a fair proportion of the crystals, it is necessary to allow small quantities of a moderately concentrated solution of the acid to evaporate in the air; if large quantities of the solution are used, the evaporation proceeds so slowly that most of the acid has decomposed when the evaporation is finished. The evaporation should proceed under a beaker, not in a desiccator.

Observations on the Concentration of Aqueous Solutions of Permanganic Acid.

In 100 c.c. of the most concentrated solution of permanganic acid which I obtained there were 16·8 grams of $HMnO_4$; this solution deposited a very small quantity of brown solid matter when kept for a few minutes in a glass vessel.

The following data give indications of the rate of decomposition of aqueous solutions of permanganic acid, of different concentrations, kept in small, corked flasks at a temperature varying from 10° to 18°.

Grams of $HMnO_4$ in 100 c.c. of solution.		Proportion of $HMnO_4$ decomposed.
At beginning of experiment	8·6	—
After 3 days	7·2	Approximately 16 per cent.
,, 5 ,, ...	7·0	,, 18 ,,
,, 8 ,, ...	6·9	,, 20 ,,
,, 12 ,, ...	6·6	,, 23 ,,
,, 24 ,, ...	6·4	,, 25 ,,
,, 48 ,, ...	5·5	,, 26 ,,
At beginning of experiment	0·37	—
After 20 days	0·29	Approximately 22 per cent.
,, 58 ,, ...	0·22	,, 40 ,,
At beginning of experiment	0·077	—
After 20 days	0·072	Approximately 6·5 per cent.
,, 58 ,, ...	0·052	,, 32 ,,

A solution containing 16·8 grams of permanganic acid in 100 c.c., mixed with brown solid matter which had deposited, when kept in a sealed tube in the dark, was found after two months to be entirely decomposed to a black solid and a colourless liquid; on opening the tube there was an outrush of oxygen.

A solution containing between 16 and 17 per cent. of the acid, free from solid matter, was kept in a sealed tube in the dark for three months; a considerable quantity of brown solid matter had then deposited; on opening the tube there was no outrush of oxygen, but the air in the tube contained more oxygen than ordinary air; the solution, when filtered, contained 7·2 per cent. of permanganic acid.

A solution containing 0·05 gram of permanganic acid in 100 c.c. can be boiled for a few minutes before separation of solid matter begins; when 0·4 gram of the acid is present in 100 c.c., deposition of solid matter begins before the boiling point is reached; when 4 grams are present in 100 c.c., a little oxygen is given off on boiling. A solution containing about 10 grams of permanganic acid in 100 c.c. (and also some brown, pasty solid) gave off ozonised oxygen at the ordinary temperature. A solution so dilute as 4 grams of the acid in

100 c.c. forms a brown film on glass on keeping in a glass vessel for half an hour. A small quantity of a solution of permanganic acid can be evaporated to dryness over a very small flame without any explosive action; the dry residue is black and contains no $HMnO_4$.

The brown, pasty solid obtained by the evaporation of a solution of permanganic acid, which is a mixture of from 30 to 44 per cent. of $HMnO_4$ with 8 to 10 per cent. of manganese oxides, and water, dissolves in pure sulphuric acid to an olive-green liquid, which deposits brown solid matter on standing and eventually becomes colourless. The addition of a few drops of water to the olive-green liquid produces a pink colour; when more water is added, the formation of brown solid matter begins. The brown, pasty solid dissolves in concentrated hydrochloric acid with the evolution of much chlorine; the addition of water to this solution causes precipitation of oxides of manganese; some manganese chloride remains in solution. Alcohol reacts violently with the brown, pasty solid with the instant formation of a black solid which is nearly pure manganese dioxide.

Compositions of the Black and Brown Solids formed by the Decomposition of Permanganic Acid.

When an aqueous solution of permanganic acid is evaporated to dryness over sulphuric acid in a vacuum, a shining, black solid is obtained. When an aqueous solution of the acid is kept in an open vessel, it gradually deposits brown, pasty solid matter. Different specimens of these solid substances were dried at 120° and analysed. The methods of analysis were these. I. Boiling with concentrated hydrochloric acid, leading the chlorine into solution of potassium iodide, and estimating the iodine by standard thiosulphate solution. II. Boiling with dilute sulphuric acid and standard oxalic acid solution, and estimating the residual oxalic acid by standard permanganate solution. III. Making direct determinations of the water in the specimens, and determining the loss of weight produced by heating to redness.

The composition of the black solid was found to agree almost exactly with that expressed by the formula $x\mathrm{MnO_2},y\mathrm{MnO}$, where $x = 20$ and $y = 1$. The composition of the brown solid varied somewhat and approached that expressed by the formula given above, when $x = 20$ and y has a value varying from 6 to 10.

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CXLI.—*The Structure of Carbonium Salts.*

By Frank Baker.

During the last five years a considerable amount of experimental work has been performed with the object of determining the constitution of the so-called carbonium salts and of the triphenylmethane dyes.

It was suggested by Baeyer (*Ber.*, 1902, **35**, 3013) that the magentas might possess the same structure as the coloured salts obtained by him from various derivatives of triphenylcarbinol, and although, in later work on the same subject, Baeyer has proposed a formula for pararosaniline, based on the assumption of a similarity in constitution between these two series of compounds, no definite proof of this assumption has been presented.

It therefore appeared possible that, as in the case of the hydrazones (Baly and Tuck, Trans., 1906, **89**, 982) and of the hydroxyazo-compounds (Tuck, Trans., 1907, **91**, 449), spectroscopic methods might prove of service in determining the structure of these substances, and I have therefore observed the spectra of some of these carbonium salts and compared them with those of pararosaniline and of its hydrochloric acid derivatives.

The first compounds of which the absorption spectra were observed were benzylidene- and dibenzylidene-acetone and their *p*-methoxy-derivatives.

The curves for dibenzylideneacetone, benzylideneanisylideneacetone, and dianisylideneacetone in solution, both in alcohol and in sulphuric acid, are shown in Figs. 1 and 2.

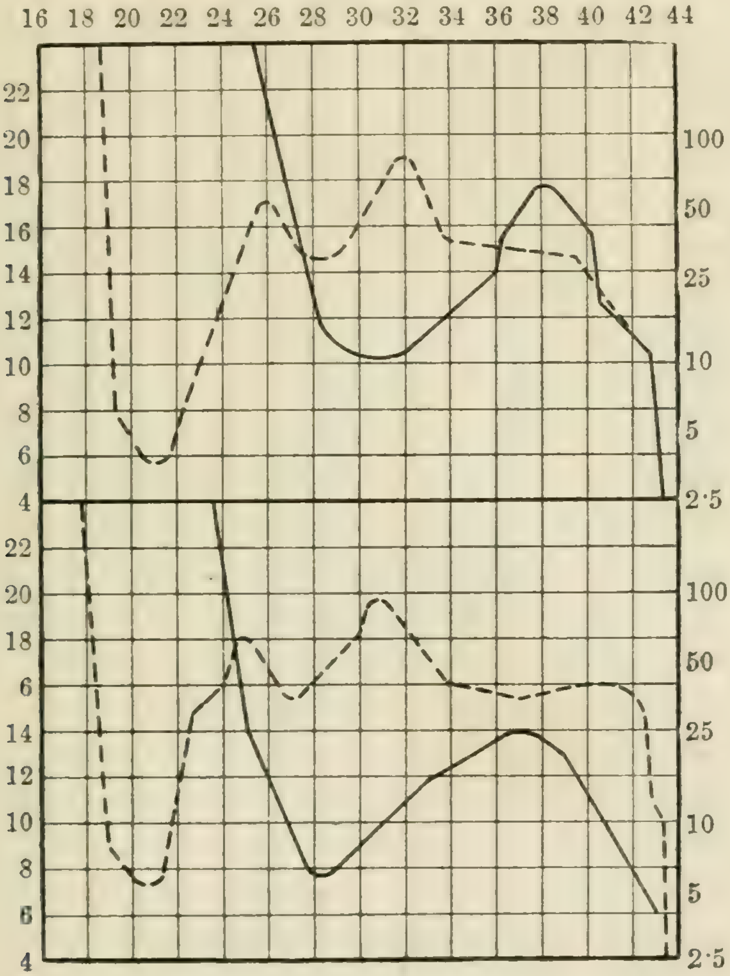
In alcohol all three substances give merely one wide band, somewhat resembling that of benzaldehydephenylhydrazone (Baly and Tuck, *loc. cit.*).

The oscillation frequency of the head of the band in the spectrum of dibenzylideneacetone is 3070; in that of the monomethoxy-derivative, 2850, and in that of the dimethoxy-compound, 2750, thus showing that in these compounds the band is moved towards the red by the introduction of heavier groups into the molecule.

When the spectra of the solutions of these substances in sulphuric acid are observed, entirely different results are obtained. In the case of dianisylideneacetone, three distinct bands are observed, two in, or near, the visible region of the spectrum, and a third in the ultraviolet. When, as in benzylideneanisylideneacetone, only one methoxy-group is introduced into the dibenzylideneacetone nucleus, it is found that the persistence of this band in the ultraviolet is greatly diminished, whilst in dibenzylideneacetone itself the band appears merely as a rapid extension of the spectrum.

From the fact that this sudden extension may be regarded as an absorption band of small persistence, it is obvious that the presence of the methoxy-groups in the dianisylideneacetone molecule is in no way the initial cause of the band, and it thus appears certain that the sulphuric acid salt of the dianisylidene compound must possess the same structure as that of dibenzylideneacetone.

FIG. 1.



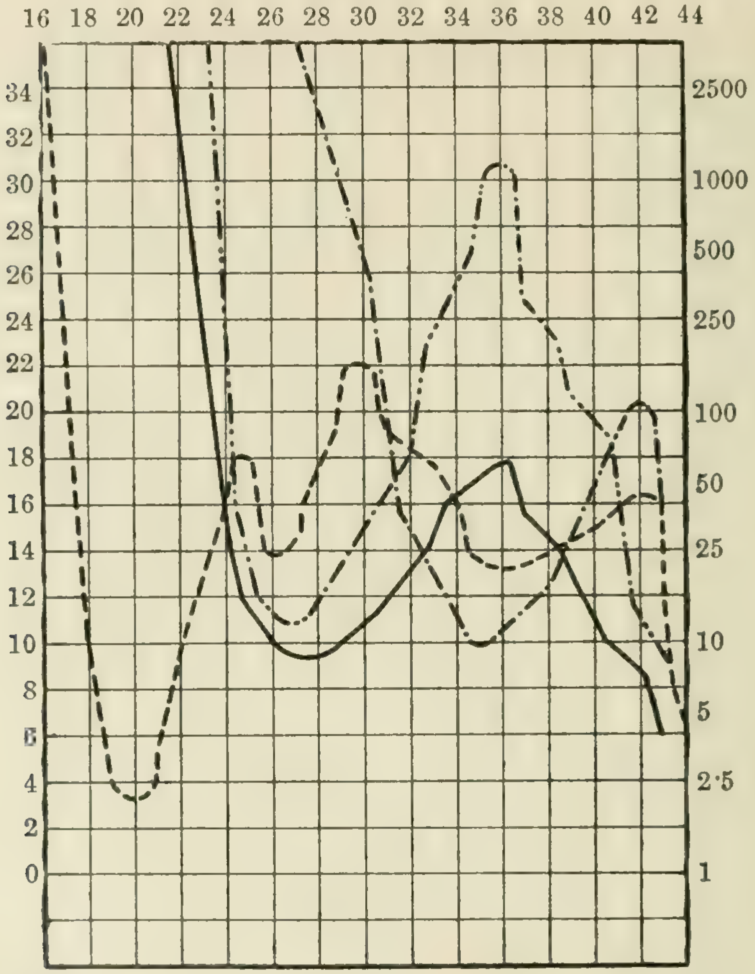
Upper curves: *Dibenzylideneacetone.*
Lower ,, *Benzylideneanisylideneacetone.*
Dotted ,, *Solutions in concentrated* H_2SO_4.

It has previously been shown in the case of the simple ketones (Stewart and Baly, Trans., 1906, **89**, 489) that the persistence of the absorption bands shown by these compounds represents the extent of the tautomeric process to which these bands are due. The tautomeric process, which is the cause of the formation of this band in the spectrum of dibenzylideneacetone, thus takes place to a considerably greater extent in the sulphuric acid solution of dianisylideneacetone.

Since the introduction of the methoxy-group into dibenzylideneacetone has been shown by Baeyer and Villiger (*loc. cit.*) to have a considerable effect on the basicity of the compound, it appears probable that this band in the ultraviolet is due to the tautomeric process

colourless variety ⇆ coloured variety,

FIG. 2.



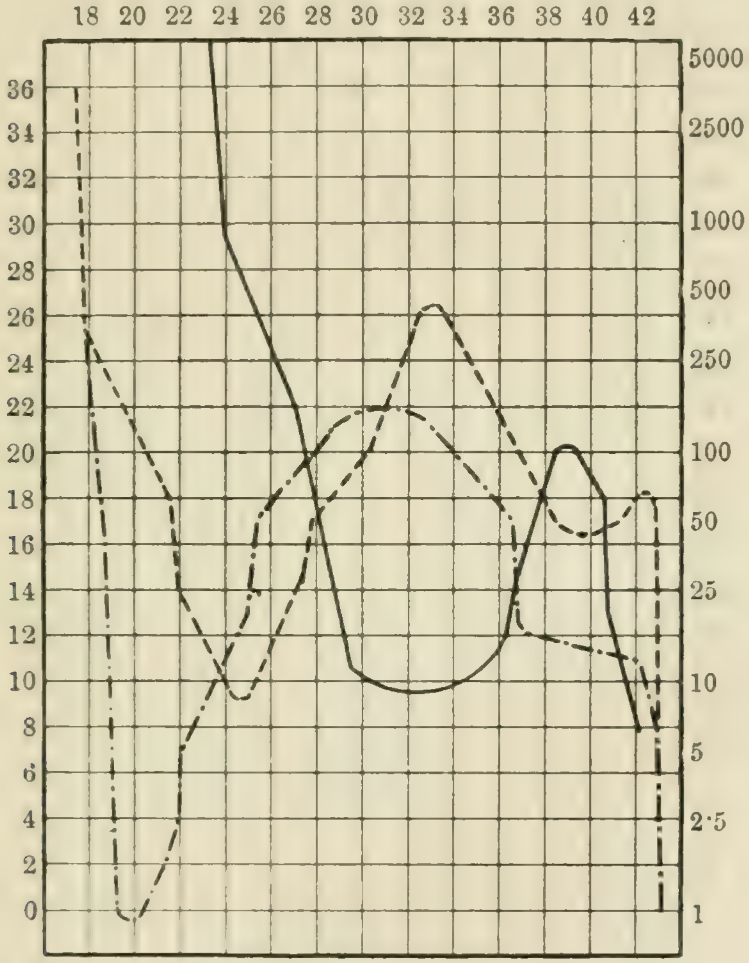
Full curve: *Dianisylideneacetone.*
Dotted ,, ,, *in concentrated* H_2SO_4.
Dash and dot curve: *Benzylideneacetone.*
Dash and two dots curve: *Benzylideneacetone in concentrated* H_2SO_4.

and that the basicity is conditioned by the extent to which this process takes place.

The absorption curves shown by benzylidene- and anisylideneacetone, both in alcoholic and in sulphuric acid solution, are shown in Figs. 2 and 3, and possess characteristics somewhat similar to those described above. In alcohol the spectra of both compounds exhibit a band of the same type as that shown by the dibenzylideneacetone, the oscillation frequencies of the bands being 3500 and 3250 respectively.

The solutions of both substances in sulphuric acid show a band of great persistence in the visible portion of the spectrum, whilst the absorption curve of anisylideneacetone also showed a band in the ultraviolet. The origin of this band is probably the same as in the previously investigated series of compounds, with the difference that dibenzylideneacetone does not give rise to such a well defined extension in the ultraviolet as does dibenzylideneacetone in sulphuric acid.

FIG. 3.

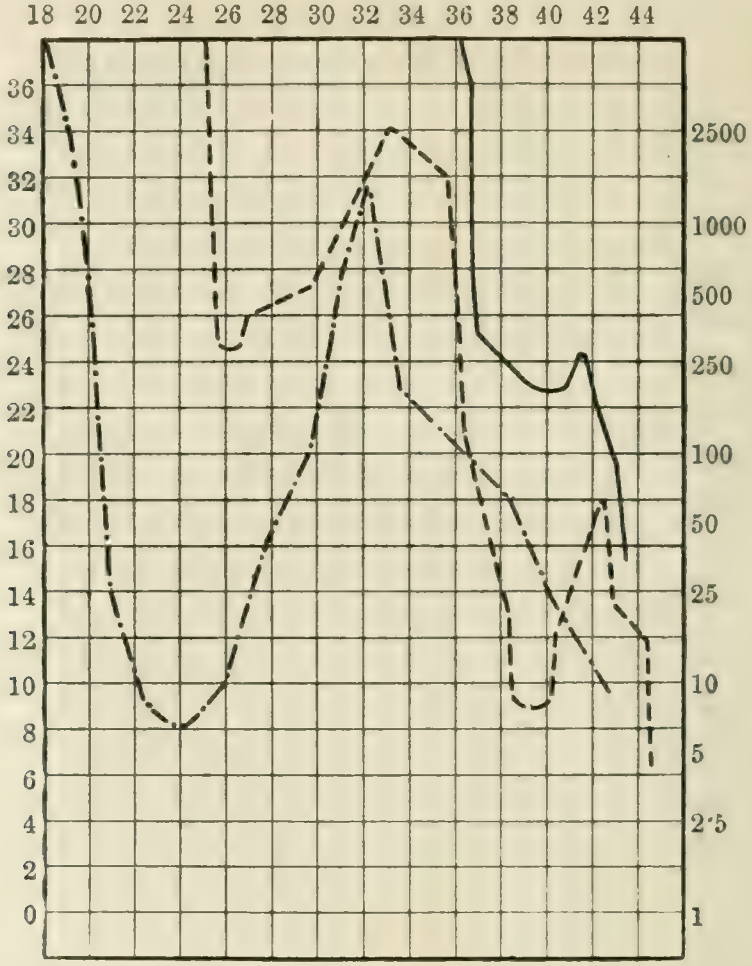


Full curve: *Anisylideneacetone in alcohol.*
Dotted ,, ,, *in concentrated* H_2SO_4.
Dash and dot curve: *Trianisylcarbinol sulphate.*

The next group of compounds to be examined was that of triphenylmethane and some of its derivatives. The absorption spectrum of triphenylmethane itself has been described by Hartley (Trans., 1887, **51**, 152), who observed two bands in the ultraviolet with oscillation frequencies of 2650 and 3930 respectively. The curve obtained by Hartley, plotted according to the logarithmic scale described by Baly and Desch (Trans., 1904, **85**, 1029), is shown in Fig. 4.

The first sample of triphenylmethane of which the absorption spectrum was determined gave, at a concentration of *N*/20, absorption bands with heads at the frequencies of 2590, 2740, 2890, 3000, and 3175.

Fig. 4.



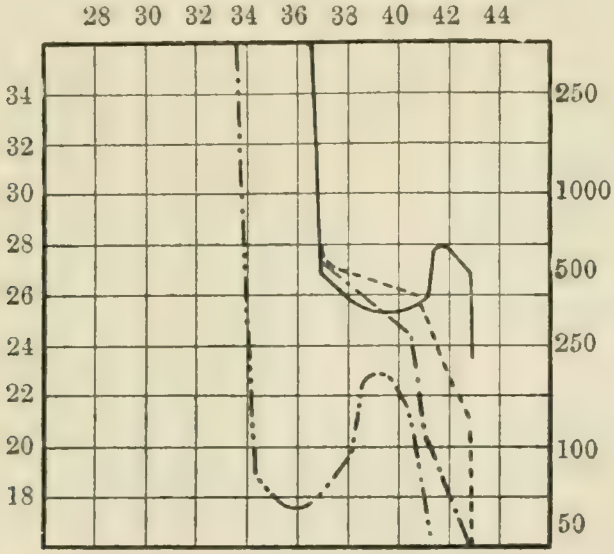
Full curve: *Triphenylmethane.*
Dotted ,, ,, (Hartley).
Dot and dash curve: *Triphenylcarbinol sulphate.*

These bands, although similar to those of anthracene, differ slightly from them in position, whilst that at the frequency of 3175 does not appear in the spectrum of anthracene. These bands, however, did not appear after the substance had been twice crystallised from alcohol; 70 mm. of a solution of *N*/20 concentration of the recrystallised compound transmitting all rays as far as $\frac{1}{\lambda} = 3565$.

Finally, a sample of triphenylmethane was prepared by means of the Friedel and Crafts reaction from thiophene-free benzene and carefully purified chloroform. The product was then submitted to a further purification by treating with sulphuric acid, according to the method described by Ullmann (*Ber.*, 1902, **35**, 1812), and crystallised several times from benzene. The crystalline benzene compound thus obtained was then heated on the water-bath until all the benzene had been expelled and the colourless residue crystallised several times from alcohol. The absorption curve of this pure compound was observed and is shown in Fig. 4.

It appeared to be possible that the results previously obtained were due to the presence of diphenylmethane as an impurity. A sample of this compound was therefore prepared and purified by a method similar to that employed in the case of triphenylmethane. The absorption spectrum is shown in Fig. 5, and it is obvious that the preceding results could not be ascribed to the presence of diphenylmethane in the substance investigated.

FIG. 5.



Full curve: *Diphenylmethane.*
Dotted ,, *Triphenylcarbinol.*
Dot and dash curve: *Triphenylchloromethane.*
Dash and two dots curve: *Trianisylmethane.*

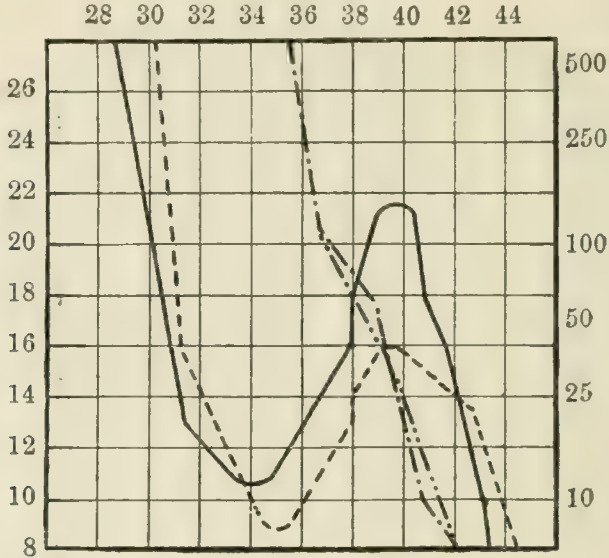
The effect of substitution of the methane hydrogen atom in triphenylmethane on the absorption spectrum is shown by the curves obtained from solutions of triphenylchloromethane and of triphenylcarbinol.

These results, which are shown in Fig. 5, prove that this substitution causes the persistence of the triphenylmethane band to be diminished to such an extent that it becomes merely a rapid extension of the spectrum; this extension being less marked in the case of the chloro-derivative.

Trianisylmethane has an absorption spectrum similar to that of triphenylmethane, the single absorption band observed being nearer the red end of the spectrum in the methoxy-compound, owing to the increased mass of the molecule.

The foregoing results have shown that when two or three phenyl groups are connected by means of a carbon atom the vibrations of the benzene rings are greatly modified. It appeared to me that two or three benzene nuclei joined together by a nitrogen atom might exhibit a similar phenomenon. I have therefore examined the absorption spectra of diphenylamine and triphenylamine, and the curves thus obtained are shown in Fig. 6. It is at once evident that there is a marked difference between the phenyl derivatives of methane and of ammonia in this respect.

FIG. 6.



Full curve: *Triphenylamine.*
Dotted ,, *Diphenylamine.*
Dash and dot curve: *Hexaphenylethane.*
Dash and two dots curve: *Carbinol from hexaphenylethane.*

In the hope of obtaining some evidence towards the determination of its constitution, I observed the absorption spectrum of the hydrocarbon which was regarded by Ullmann and Borsum (*Ber.*, 1902, **35**, 2877) as hexaphenylethane, and also the spectrum of the carbinol derived from it (Tschitschibabin, *Ber.*, 1904, **37**, 4709).

The results obtained, which are shown in Fig. 6, are not, however, sufficiently characteristic to enable any definite conclusions to be drawn.

The absorption spectra of the sulphates of triphenyl- and trianisylcarbinol, which were next investigated, are shown in Figs. 3 and 4.

The curves of both substances show a band in the visible region of the spectrum, the oscillation frequency of the head of the band of triphenylcarbinol sulphate being 2400, whilst the band shown by the trianisyl compound, in accordance with the general law, is considerably nearer the red end of the spectrum, the vibration frequency of its head being 1980.

Although the concentration at which the band appears is somewhat different in the two cases, the persistence of the band is practically the same in these two curves and is approximately equal to the persistence of the band shown by the sulphuric acid solution of benzylideneacetone.

The curve given by triphenylcarbinol sulphate shows a fairly rapid extension in the ultraviolet, but no definite evidence of tautomerism has been observed.

Trianisylcarbinol, in sulphuric acid solution, shows a marked extension of the spectrum at a mean oscillation frequency of 3950. It has been shown (Baeyer and Villiger, *Ber.*, 1902, **35**, 3015) that the introduction of methoxy-groups into the triphenylcarbinol nucleus has an effect on the basicity similar to that observed in the dibenzylideneacetone series, and it is also seen that the effect which this substitution produces on the absorption spectra of the sulphuric acid compounds is similar in the two cases.

It is evident, therefore, that the carbonium salts investigated give rise to two types of spectra, which we may term the dibenzylideneacetone and the triphenylcarbinol types.

The absorption spectrum of pararosaniline hydrochloride, as well as that of the free base, shows a band in the visible region of the spectrum (Fig. 7.), the persistence of this band in both cases being the same as that given by triphenylcarbinol sulphate. Both compounds give rise to an absorption band in the ultraviolet at a frequency of 3480, but the depth of this band in the spectrum of the hydrochloride is considerably greater than in that of the free base.

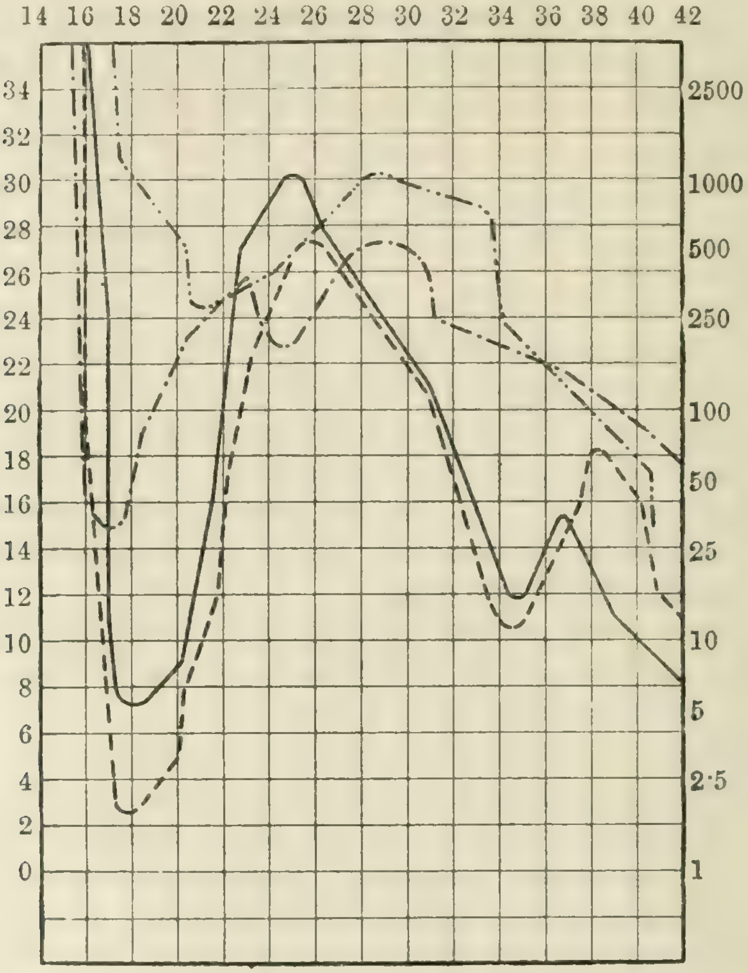
This is probably due to the tendency of the colourless compound to pass into the coloured modification, being considerably greater in the case of the hydrochloride.

The previously observed spectra of rosaniline (and its hydrochloride) (Hartley, *loc. cit.*) when plotted on a logarithmic scale show precisely the same phenomenon, whilst the persistence of the colour band in rosaniline and also in Methyl-violet is practically the same as in pararosaniline. In presence of a fairly large excess of acid, the absorption shown by this substance undergoes considerable change. The curve obtained in presence of normal hydrochloric acid is very similar to that shown by dibenzylideneacetone in concentrated sulphuric acid.

It is thus seen that pararosaniline can give rise to both the above-mentioned characteristic types of absorption spectra, and we may therefore legitimately conclude that the pararosaniline salts are carbonium compounds.

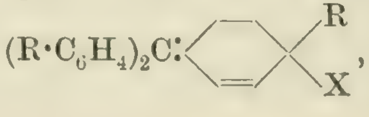
Trianisylcarbinol is a much stronger base than triphenylcarbinol (Baeyer and Villiger, *loc. cit.*). The methoxy-group, however, is only feebly basic in character, and it is obvious that the introduction of the more basic amino-group into the molecule in place of the methoxy-group would increase the basicity to an enormously greater extent.

FIG. 7.

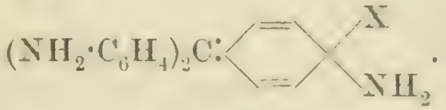


Full curve: *Pararosaniline.*
Dotted ,, *Pararosaniline hydrochloride.*
Dash and dot curve: *Pararosaniline in* N*-hydrochloric acid.*
Dash and two dots curve: *Pararosaniline in conc. hydrochloric acid.*

Assuming that the coloured salts of triphenylcarbinol and its para-derivatives exist in the quinonoid form



I therefore regard the constitution of the salts of pararosaniline with one equivalent of acid as



The formula given above will readily explain several of the properties of the magentas which are difficult of explanation by means of any other structure; the existence of a stable tetrachloride and the existence at low temperatures of a heptachloride are readily accounted for in this way.

Further, iminoquinone has recently been prepared (Willstätter, Mayer, and Pfannenstiehl, *Ber.*, 1904, **37**, 1891) and found to be colourless, whilst the same has been observed in the case of iminocamphorquinone (Forster and Fierz, Trans., 1905, **87**, 826). These observations, together with the known instability of such imino-compounds in presence of acids, render the iminoquinone formula of Nietzki extremely improbable.

The constitution proposed above, on the contrary, is not open to these objections, and this may be regarded as strengthening the theory which I have brought forward.

The curve for pararosaniline, when plotted in the normal manner, shows a discontinuity on dilution; for example, the band in the ultraviolet appears and is complete at the two concentrations $N/1000$ and $N/10,000$. The differences between the ordinates of the heads of the bands, when plotted in this manner, show that the concentration of the compound to which this spectrum is due, instead of decreasing to one-tenth of its value on dilution, only falls to 0·21 of its original amount. This indicates that we are dealing with a state of equilibrium which is not entirely unimolecular, and corresponds with the assumption that in alcoholic solution the carbonium hydroxide, itself only present to a small extent, dissociates, forming the ions

$$(C_6H_5\cdot NH_2)_2C:C_6H_4:\overset{+}{N}H_2 \text{ and } \overset{-}{O}H.$$

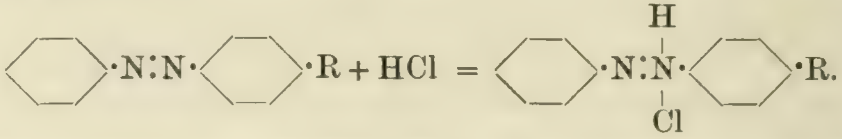
The conductivity of pararosaniline in alcoholic solution was next determined, and the following results obtained.

Volume in which 1 grm.-mol. was dissolved.	Molecular conductivity.
400 litres	2·42
800 ,,	3·38
3200 ,,	7·62
6400 ,,	9·63
12800 ,,	12·4

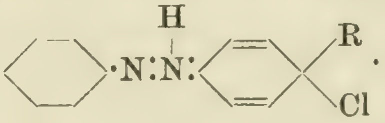
The increase in value of molecular conductivity, as well as the discontinuity in the spectrum curve, shows that the colour and the conductivity cannot be due to traces of the hydrochloride or other salt of pararosaniline. These results therefore prove that pararosaniline in alcoholic solution is slightly ionised, behaving as the hydroxide of a free base.

The absorption spectra of the derivatives of dibenzylideneacetone in sulphuric acid solution bear a striking resemblance to those of certain members of the hydroxyazo-group of compounds (Tuck, *loc. cit.*). These spectra were found to be entirely different from those shown by the parent compounds, and it thus appears probable that these compounds are also carbonium salts, and are formed in a manner precisely similar to that in which the coloured derivatives of dibenzylideneacetone were obtained.

The addition of hydrochloric acid probably takes place in the following manner:



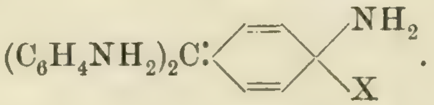
This hydrochloride then passes into the tautomeric quinonoid form:



Conclusions.

(1) The sulphates of the methoxy-derivatives of dibenzylideneacetone and triphenylcarbinol possess structures similar to those of the salts of the parent compounds.

(2) Pararosaniline salts are carbonium compounds of the same type as triphenylcarbinol sulphate, and thus possess the formula:



(3) In alcoholic solution, pararosaniline possesses the properties of a weak basic hydroxide.

(4) The hydrochlorides of the hydroxyazo-compounds and their ethers are also carbonium salts.

I wish to express my thanks to Mr. Baly and Dr. Smiles for the interest they have taken in this research, and also to the former for affording me facilities for carrying out the experimental work.

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CXLII.—*A New Colouring Matter from Nyctanthes Arbor-tristis.*

By Ernest George Hill and Annoda Prasad Sirkar.

The *Nyctanthes Arbor-tristis* (Urdu, *harsinghar*) is a large shrub of the order Oleaceæ. The flowers are sessile in bracteate fascicles, pedunculate, and arranged in short terminal trichotomous cymes; the corolla tube is orange and the limb white. The flowers open at night and fall to the ground the following day. They are then collected for use in dyeing. The plant grows abundantly in the sub-Himalayan districts.

For dyeing purposes the flowers are boiled in water and the solution is strained off. This is a beautiful golden-yellow colour and dyes cotton without a mordant. The effect is transitory, the colour fading slowly, although when used with alum and lime-juice the colour is brighter and more permanent. It is used chiefly in combination with turmeric and safflower, and sometimes with indigo and *Butea frondosa*.

Aqueous Extract.—The flowers were well soaked in cold water and the extract filtered. In concentrated solutions this was dark brown, but on dilution it became golden-yellow. It has a slightly sweet and bitter taste. The infusion gave a slightly acid reaction with litmus. With basic lead acetate it gave a yellow precipitate, unaffected by ammonia; with copper sulphate, a pale yellow precipitate which became green with ammonia; with ferric chloride a greenish-black colour which darkened on adding ammonia. The infusion reduced Fehling's solution, gold chloride and ammoniacal silver nitrate. It gave no reaction with a solution of gelatin. When a few drops were added carefully to a similar amount of concentrated sulphuric acid, an intense blue colour was produced at the junction of the two liquids; this soon darkened and disappeared on shaking.

When the aqueous extract was warmed to about 70° with a few drops of hydrochloric acid, a red, flocculent precipitate separated which attained its maximum in about twelve hours. When the solution was boiled, or heated on the water-bath, the precipitate formed was darker at first, and finally a black, amorphous substance was precipitated. This was very light and friable when dry.

When the infusion was precipitated by means of basic lead acetate, and the washed precipitate decomposed by hydrogen sulphide, a yellow solution was obtained which, on warming, gave a red, flocculent precipitate similar to that obtained by heating the infusion with dilute hydrochloric acid at 70°.

As the second method appeared to have no advantage over the first one, a considerable quantity of the solution was warmed with a little hydrochloric acid and left in a warm place for several days. The precipitate was collected and the filtrate again left for several days. Very little more colouring matter separated, but on boiling the solution a black powder similar to that described above was formed. On removal of this the solution was evaporated on a water-bath and the residue dissolved in a little water and filtered. The filtrate had a sweet taste and reduced Fehling's solution.

The coloured precipitate obtained by this hydrolysis was washed with water and boiled with alcohol. A large part of it dissolved, but there remained a considerable highly coloured residue. This was redder than the original precipitate and left more ash on combustion. It was at first thought that the insoluble portion was a salt of the colouring matter, but this was found not to be the case.

The solution in alcohol was evaporated to dryness and gave a dark red, lustrous deposit, which entirely redissolved in alcohol. It melted between 250° and 260°; was soluble in ethyl acetate, ether, alkalis, alkali carbonates, or in a solution of borax. It was sparingly soluble in chloroform and insoluble in benzene. In cold water it was insoluble, but dissolved slightly on boiling. The colouring matter thus obtained could not be crystallised from any of the solvents enumerated. On analysis of several samples obtained by the same method only fair agreement in the percentage composition was shown, and it always appeared that the redder the product the less oxygen and the more hydrogen was present in the sample.

As it seemed possible that hydrolysis might be incomplete, some of the alcoholic solution was boiled with a few drops of hydrochloric acid, when a bright scarlet precipitate was formed. This was collected and found to be entirely different from the original precipitate; it was brighter, much more friable, and insoluble in alcohol. It was also found to crystallise from pyridine and phenylhydrazine.

Alcoholic Extract.—Since much of the colouring matter in the flowers appeared soluble in alcohol, it was thought worth while to extract them with alcohol in a modified form of Soxhlet's apparatus. This was done until the flowers were colourless, when fresh flowers were exchanged for them. The concentrated solution in alcohol was allowed to cool, and bunches of needle-shaped crystals were deposited on the walls of the flask. On recrystallisation these crystals, which were bright yellow at first, became white. They had a sweet taste, reduced ammoniacal silver nitrate, and had no effect on polarised light, but when borax was added to the solution it became dextrorotatory. The crystals were very soluble in water and soluble in hot alcohol, from which they separated in delicate needles melting at 166°. On analysis:

C = 39·62; H = 7·96.

$C_6H_{14}O_6$ requires C = 39·57; H = 7·7 per cent.

The crystals were thus identified as mannitol, which melts at 168°.

The alcoholic solution of the colouring matter obtained by this extraction was warmed with a little hydrochloric acid, and the bright scarlet precipitate was produced just as in the case above. The amount formed both from the aqueous extract and alcoholic extract was very small, but for the preparation of a sufficient quantity for analysis the method of aqueous extraction was preferable. The preparation was extraordinarily tedious and slow. Enormous quantities of solution had to be prepared, and the filtration of the precipitate after treatment with hydrochloric acid was difficult owing to its gelatinous and sticky nature. It was found that flowers of the previous year which had been kept through a monsoon gave practically no red substance, but a dark deposit when heated with acid.

It was also found that the portion of the precipitate which did not dissolve in alcohol contained some of the colouring principle which could be crystallised from pyridine. As this precipitate also contained mineral matter and apparently albuminoids, it was not easy to obtain a pure yield of the crystals from it. The crystals are very soluble in pyridine, and their purification was attended by considerable loss.

For the preparation of a sufficient quantity of the pure crystalline product, the method adopted was to add about 1 per cent. of hydrochloric acid to the aqueous extract of the flowers and warm gently for several hours. The precipitate was filtered off, boiled with alcohol and again filtered, and the filtrate heated gently with about 1 per cent. of concentrated hydrochloric acid. The red colouring matter separated slowly in flakes which were collected, washed first with alcohol, then with water, and finally crystallised from pyridine or phenylhydrazine and dried on porous porcelain. They were then kept in a steam oven for several hours. Although the aqueous extract was very highly coloured, it was necessary to prepare many gallons of it in order to collect 2 or 3 grams of the crude red product.

The crystals from pyridine were regular hexagons which were yellow while wet, but of a brick-red colour when dry. The crystals from phenylhydrazine were the same colour, but rhombic in shape. Both were microscopic in size. Those from pyridine melted between 225° and 230°. They dissolved in alkalis to form a yellow solution from which the red substance was reprecipitated by acids. The crystals were practically insoluble in water; very sparingly soluble in ether, benzene, alcohol, or light petroleum; moderately so in toluene, and readily so in pyridine or phenylhydrazine. With a drop of sulphuric acid they gave a most intense blue colour which rapidly turned yellow. The crystals from pyridine gave the following results on analysis:

I. 0·1755 gave 0·4669 CO_2 and 0·1311 H_2O. C = 72·51; H = 8·35.
II. 0·1119 „ 0·2985 CO_2 „ 0·0830 H_2O. C = 72·71; H = 8·29.
III. 0·1554 „ 0·4148 CO_2 „ 0·1120 H_2O. C = 72·76; H = 8·06.

Nos. I and II were from the same preparation, No. III from a different one.

The crystals from phenylhydrazine were also analysed:

IV. 0·1290 gave 0·3440 CO_2 and 0·0948 H_2O. C = 72·68; H = 8·22.
V. 0·1210 „ 0·3226 CO_2 „ 0·0896 H_2O. C = 72·68; H = 8·28.

Nos. IV and V were from different preparations.

The crystals from phenylhydrazine have thus the same composition as those from pyridine. The mean of the five analyses gives C = 72·67; H = 8·24.

$C_{20}H_{27}O_4$ requires C = 72·44; H = 8·21 per cent.
$C_{15}H_{20}O_3$ „ C = 72·51; H = 8·12 „

Acetyl Compound.—One part of the crystals from pyridine was mixed with four times its weight of acetic anhydride and boiled for twenty-four hours, using a reflux condenser. On gentle evaporation of the acetic anhydride, a dark red powder separated which had no crystalline form, but which formed in nodular clusters on the sides of a flask when the hot solution was allowed to cool. This red amorphous substance no longer crystallised from phenylhydrazine or pyridine.

The products of the reaction were poured into cold water, and the acetyl compound was washed free from acid and dried in a steam oven. It could not be obtained in the crystalline condition, separating as an amorphous powder from ethyl acetate or alcohol, as well as from pyridine or phenylhydrazine, in all of which it was soluble. On analysis:

0·1211 gave 0·3118 CO_2 and 0·0862 H_2O. C = 70·18; H = 7·96.
0·1083 „ 0·2796 CO_2 „ 0·0770 H_2O. C = 70·37; H = 7·95.

$C_{20}H_{26}O_4{\cdot}C_2H_3O$ requires C = 70·71; H = 7·83 per cent.
$C_{15}H_{19}O_3{\cdot}C_2H_3O$ „ C = 70·28; H = 7·64 „

Two other samples of the acetyl compound prepared by a similar method were boiled with barium hydroxide in a reflux apparatus. The filtered product was treated with excess of carbon dioxide and the filtrate evaporated to dryness. The residue was extracted with water and filtered, and the barium estimated as sulphate:

I. 0·1688, on hydrolysis, gave 0·0570 $BaSO_4$. $C_2H_3O = 12·5$.
II. 0·6380 „ „ 0·2154 $BaSO_4$. $C_2H_3O = 12·48$.
$C_{15}H_{19}O_3·C_2H_3O$ requires $C_2H_3O = 14·8$ per cent.
$C_{20}H_{26}O_4·C_2H_3O$ „ $C_2H_3O = 11·5$ „

As this method of estimating acetyl groups tends to give a slightly high value, the probable formula for the derivative is $C_{20}H_{26}O_4·C_2H_3O$, and for the red crystalline colouring matter $C_{20}H_{26}O_3·OH$.

Since the red crystals dissolve in acetic anhydride, a small quantity in this solvent was examined for methoxyl and similar groups by Zeisel's method, but with a negative result.

From the fact that phenylhydrazine acts simply as a solvent, it would appear that no ketonic groups exist in the molecule. No action was observed with hydroxylamine.

On fusing with potassium hydroxide at 210° for several hours, the colour of the crystals was destroyed. On cooling the product and examining in the usual manner for phloroglucinol, none was found. The purified product, after neutralisation and extraction with ether, was so small that it could not be analysed. It did not give the usual reactions of pyrocatechol; ferrous sulphate coloured the solution violet, but ferric chloride gave no distinctive reaction.

On bromination of the product obtained by warming the aqueous extract of the flowers with hydrochloric acid, a brown amorphous powder was obtained which could not be crystallised. This gave off bromoform when heated with potassium hydroxide. Analysis gave:

$C = 25·5$ and $25·0$; $H = 1·5$ and $1·7$; $Br = 41·1$ and $42·1$.
$C_{20}H_{15}O_{18}Br_5$ requires $C = 25·2$; $H = 1·56$; $Br = 42·4$ per cent.

Although the substance $C_{20}H_{27}O_4$ appeared to be acid in character, no salt could be isolated from the small amount of substance available for these experiments. It appears to contain one hydroxyl group and one or more methyl groups. The name *nyctanthin* is suggested for it.

ALLAHABAD.

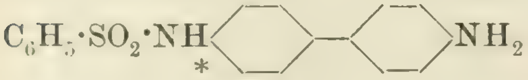
CXLIII.—*The Diazo-derivatives of Benzenesulphonylbenzidine.*

By GILBERT T. MORGAN and JAMES MORTON HIRD.

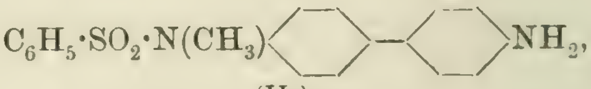
THE study of diazonium salts has recently received a fresh impetus, owing to the circumstance that a new formulation has been put forward for aromatic diazo-compounds which aims at explaining the relationships existing between these substances without recourse to the stereochemical hypotheses, somewhat arbitrarily adopted to account for the existence of isomerism in this series. The formula for diazonium salts advocated by Cain (this vol., p. 1049) assumes a quinonoid rearrangement of the aromatic nucleus, while the salt-forming nitrogen of the diazo-complex retains its quinquevalency and thus conforms to the ammonium theory of saline nitrogen compounds.

One of the authors has pointed out (Proc., 1907, **23**, 160, and this vol., p. 1314) that that part of the hypothesis which relates to the quinonoid structure accords with the fact that, although many of the simpler diazonium salts are colourless, yet certain of the more complicated members of this group are distinctly coloured. Two opinions are now held with regard to these coloured diazonium salts; on the one hand, they are assumed to have a constitution essentially different from that of the colourless diazo-compounds, whereas, on the other, both coloured and colourless salts are supposed to have the same configuration, and the appearance of colour is attributed to the presence of a complex group in the second quinonoid position with respect to the salt-forming nitrogen atom, and also in some degree to the nature of the aromatic portion of the molecule.

The experiments recorded in this paper have been made with the object of deciding between these two opinions. The diazonium halides of benzenesulphonylbenzidine (I) and as-*benzenesulphonylmethylbenzidine* (II),



(I.)

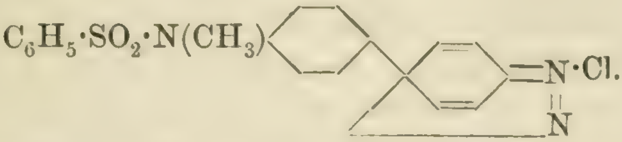


(II.)

have been found to be coloured, although in the case of the latter base the labile hydrogen (*) has been replaced by methyl. This substitution appreciably diminishes the colour of these salts, but does not render them colourless. The diazonium chloride and bromide of the unmethylated base (I) are orange-coloured compounds, whilst the corresponding salts derived from the methylated base (II) are yellow. The diazonium sulphate of the first base is yellow, whereas that of the second is almost colourless and has only a faint yellow tinge.

On the view that the coloured diazonium salts have a constitution differing from the colourless compounds of this series, those derived from benzenesulphonylbenzidine would be represented by the formula $C_6H_5{\cdot}SO_2{\cdot}N{:}C_6H_4{:}C_6H_4{:}NCl{:}NH$. A structural formula of this type is, however, inapplicable to the diazo-derivatives of the methylated

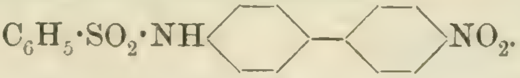
base, which are accordingly regarded as having the following constitution :



The benzenesulphonyldiphenyldiazonium salts, when treated with either aqueous sodium acetate or potassium hydrogen carbonate, furnished a brown, crystalline substance which has the composition of a diazoimide combined with two molecules of water. When carefully heated at 105°, this compound assumed a brownish-yellow colour, and lost both its water and the whole of its diazo-nitrogen. The anhydrous diazoimide was not obtained.

EXPERIMENTAL.

4′-*Benzenesulphonylamino*-4-*nitrodiphenyl*,



—4 : 4′-Dinitrodiphenyl was prepared by Willstätter and Kalb's method (*Ber.*, 1906, **39**, 3478), in which *p*-nitrobenzenediazonium chloride is reduced by means of a cuprous salt. In this way, 40 grams of the dinitro-compound were obtained from 138 grams of *p*-nitroaniline.

4-Nitro-4′-aminodiphenyl was produced by reducing the dinitro-compound with alcoholic ammonium sulphide, 12 grams of the substance being dissolved in 700 c.c. of warm alcohol and 100 grams of 25 per cent. ammonia, while hydrogen sulphide was introduced in rather more than the calculated quantity. After evaporating off the alcohol, the benzidine present was extracted with hot water, and the nitroaminodiphenyl separated from sulphur with hot dilute hydrochloric acid. The residue also contained some unaltered dinitrodiphenyl, which was extracted with glacial acetic acid. From 5 to 6 grams of nitroaminodiphenyl were set free with ammonia from the hydrochloric acid solution.

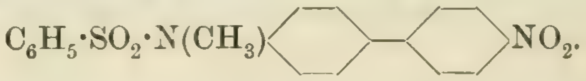
4-Nitro-4′-aminodiphenyl (6 grams) is readily soluble in dry pyridine to a red solution, which, when warmed for three to four hours with benzenesulphonic chloride (6 grams), yields 4′-benzenesulphonylamino-4-nitrophenyl in almost theoretical amount. The solution was poured into ice-water and the precipitate extracted with hydrochloric acid. The residue dissolved in hot aqueous sodium carbonate to a deep red solution, from which, on cooling, the yellow sodium salt of 4′-benzenesulphonylamino-4-nitrodiphenyl separated. On acidifying with dilute acetic acid, the free sulphonamide was deposited as an almost colourless precipitate. When recrystallised from dilute alcohol, this compound separated in yellow plates melting at 174°:

0·3343 gave 0·2268 $BaSO_4$. S = 9·32.
0·2818 ,, 20·4 c.c. nitrogen at 21° and 757 mm. N = 8·21.
$C_{18}H_{14}O_4N_2S$ requires S = 9·03; N = 7·90 per cent.

Benzenesulphonylbenzidine (compare Hinsberg, *Annalen*, 1892, **272**, 231) was prepared from the preceding compound by reduction with iron filings and hot water acidified with acetic acid; the heating was maintained for an hour, as otherwise the product was contaminated with a considerable proportion of unaltered nitro-compound. The solution was then rendered alkaline with sodium carbonate and rapidly filtered; colourless crystals separated, but by far the larger portion of the product was extracted from the iron oxide precipitate by means of alcohol, in which the base is very soluble. When prepared in this way, benzenesulphonylbenzidine was obtained in colourless needles melting at 165°, the yield being 93 per cent. of the calculated quantity:

0·2405 gave 0·1698 $BaSO_4$. S = 9·70.
0·2177 ,, 16·8 c.c. nitrogen at 21° and 757 mm. N = 8·75.
$C_{18}H_{16}O_2N_2S$ requires S = 9·87; N = 8·64 per cent.

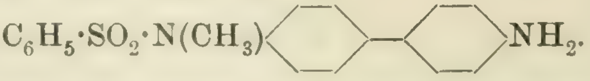
4′-*Benzenesulphonylmethylamino*-4-*nitrodiphenyl*,



—4′-Benzenesulphonylamino-4-nitrophenyl was dissolved in absolute alcohol with the calculated amount of potassium hydroxide and the solution heated for three hours with excess of methyl iodide. The filtered solution was then set aside to crystallise, when the product separated in yellow plates, the yield being almost quantitative. After crystallisation from alcohol, the compound melted at 132°:

0·4261 gave 27·5 c.c. nitrogen at 28° and 758 mm. N = 7·18.
0·2193 ,, 0·1312 $BaSO_4$. S = 8·22.
$C_{19}H_{16}O_4N_2S$ requires N = 7·60; S = 8·69 per cent.

as-*Benzenesulphonylmethylbenzidine*,



—The preceding nitro-compound was readily reduced with iron filings and very dilute acetic acid; the mixture was heated for thirty minutes, then neutralised with sodium carbonate, and rapidly filtered. A small portion of the new base separated on cooling the filtrate, but the greater part was extracted from the residue with alcohol and then precipitated from this extract with water.

as-Benzenesulphonylmethylbenzidine separated from dilute alcohol in clusters of almost colourless needles melting at 134—135° :

0·1882 gave 0·1339 $BaSO_4$. S = 9·76.
0·1863 „ 14·0 c.c. nitrogen at 22° and 763 mm. N = 8·55.
$C_{19}H_{18}O_2N_2S$ requires S = 9·46. N = 8·28 per cent.

Diazotisation of Benzenesulphonylbenzidine.

4′-*Benzenesulphonylaminodiphenyl*-4-*diazonium chloride*,
$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2Cl$.
—This salt separated as an orange, crystalline precipitate on adding alcoholic hydrochloric acid to a cold alcoholic solution of benzenesulphonylbenzidine containing a slight excess of amyl nitrite :

0·1496 gave 0·0554 AgCl. Cl = 9·16.
0·1161 „ 11·0 c.c. nitrogen at 24° and 763 mm. N = 10·66.
$C_{18}H_{14}O_2N_3ClS$ requires Cl = 9·54. N = 11·30 per cent.

The diazonium chloride is somewhat soluble in alcohol, and is precipitated from this solvent by ether. When separating slowly from dilute solutions, it forms clusters of slender, orange needles which decompose with intumescence at 121—122°.

4′-*Benzenesulphonylaminodiphenyl*-4-*diazonium bromide*,
$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2Br$,
was formed as an orange, crystalline precipitate on adding successively to an alcoholic solution of the base a slight excess of amyl nitrite and hydrobromic acid :

0·1450 gave 0·0680 AgBr. Br = 19·95.
$C_{18}H_{14}O_2N_3BrS$ requires Br = 19·23 per cent.

The salt decomposes at 124°.

4′-*Benzenesulphonylaminodiphenyl*-4-*diazonium sulphate*,
$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot HSO_4$,
was prepared from the base, amyl nitrite and sulphuric acid in glacial acetic acid solution ; it separated as a yellow, microcrystalline precipitate :

0·1671 gave 0·1688 $BaSO_4$. S = 13·88.
$C_{18}H_{15}O_6N_3S_2$ requires S = 14·78 per cent.

Benzenesulphonyldiphenyl-4 : 4′-*diazoimide*,
$C_6H_5\cdot SO_2\cdot \underline{N\cdot C_6H_4\cdot C_6H_4\cdot N}_2,2H_2O$,
was obtained by treating any of the foregoing diazonium salts with aqueous sodium acetate or potassium hydrogen carbonate as a crystalline, dark brown substance slightly soluble in cold water, which was washed successively with water, ether, and light petroleum :

0·1923 gave 0·4072 CO_2 and 0·0864 H_2O. C = 57·81 ; H = 4·99.
0·1784 „ 16·8 c.c. nitrogen at 25° and 760 mm. N = 10·85.

0·2362 gave 0·1520 $BaSO_4$. S = 8·84.

$C_{18}H_{13}O_2N_3S,2H_2O$ requires C = 58·22; H = 4·63; N = 11·32; S = 8·62 per cent.

When triturated with β-naphthol moistened with a small quantity of pyridine, the diazoimide gives rise to its azo-naphthol derivative; it regenerates the original diazonium salt on treatment with a cold mineral acid. When heated at 105°, the compound assumes a yellow colour, and at 128° it intumesces very considerably. An analysis of the yellow product showed that it contained only one-third of the nitrogen originally present in the brown compound.

Diazotisation of as-*Benzenesulphonylmethylbenzidine.*

4′-*Benzenesulphonylmethylaminodiphenyl*-4-*diazonium chloride*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2Cl$.—On adding alcoholic hydrochloric acid to an alcoholic solution of benzenesulphonylmethylbenzidine containing a slight excess of amyl nitrite, the almost colourless solution assumed a yellow colour, and on filtering and diluting with 3 or 4 volumes of ether the diazonium chloride separated in transparent, yellow needles:

0·1534 gave 0·0543 AgCl. Cl = 8·75.

0·2267 ,, 21·8 c.c. nitrogen at 22° and 763 mm. N = 10·94.

$C_{19}H_{16}O_2N_3ClS$ requires Cl = 9·19; N = 10·89 per cent.

4′-*Benzenesulphonylmethylaminodiphenyl*-4-*diazonium bromide*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2Br$.—*as*-Benzenesulphonylmethylbenzidine was dissolved in cold alcohol and treated successively with amyl nitrite and alcoholic hydrobromic acid, when a deep yellow solution was obtained, which, on mixing with several volumes of ether, deposited clusters of golden-yellow needles. This salt was washed successively with alcohol, ether, and light petroleum, and dried over quicklime:

0·1306 gave 11·7 c.c. nitrogen at 24° and 762 mm. N = 10·07.

$C_{19}H_{16}O_2N_3BrS$ requires N = 9·77 per cent.

4′-*Benzenesulphonylmethylaminodiphenyl*-4-*diazonium sulphate*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}HSO_4$, was obtained as a pale yellow, crystalline precipitate on treating a glacial acetic acid solution of *as*-benzenesulphonylmethylbenzidine with amyl nitrite and sulphuric acid:

0·1850 gave 16·0 c.c. nitrogen at 24° and 763 mm. N = 9·73.

$C_{19}H_{17}O_6N_3S_2$ requires N = 9·40 per cent.

Azo-derivatives of Benzenesulphonylbenzidine.

4′-*Benzenesulphonylaminodiphenyl*-4-*azo*-β-*naphthol*,
$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$.
—When any of the foregoing 4′-benzenesulphonylaminodiphenyl-4-diazonium salts were added to an alkaline solution of β-naphthol, a deep red liquid was obtained, which, if sufficiently concentrated, deposited a dark red, viscid substance soluble in water. This sodium derivative of the azo-β-naphthol was decomposed with glacial acetic acid and the free azo-compound crystallised from the same medium, when it separated in small, scarlet needles melting at 218—219°:

0·2234 gave 18·0 c.c. nitrogen at 23° and 760 mm. N = 9·08.
$C_{28}H_{21}O_3N_3S$ requires N = 8·77 per cent.

This azo-derivative was also obtained from benzenesulphonyldiphenyldiazoimide either by dissolving this substance in cold hydrochloric acid and coupling the resulting diazonium salt with alkaline β-naphthol or more directly by gently warming the diazoimide with β-naphthol in dry pyridine solution.

4′-*Benzenesulphonylmethylaminodiphenyl*-4-*azo*-β-*naphthol*,
$C_6H_5\cdot SO_2\cdot N(CH_3)\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$.
—This azo-derivative was produced as a brilliant scarlet precipitate when any of the 4′-benzenesulphonylmethylaminodiphenyl-4-diazonium salts were added to an alkaline solution of β-naphthol. When crystallised from glacial acetic acid, this compound separates in dark red spangles melting at 198—199°:

0·2258 gave 17·3 c.c. nitrogen at 24° and 762 mm. N = 8·61.
$C_{29}H_{23}O_3N_3S$ requires N = 8·52 per cent.

The foregoing azo-β-naphthols both develop purple-red colorations on treatment with cold concentrated sulphuric acid.

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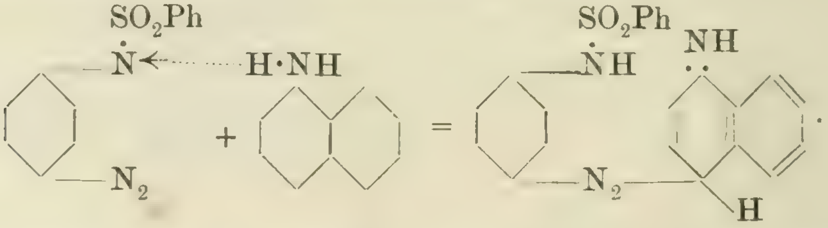
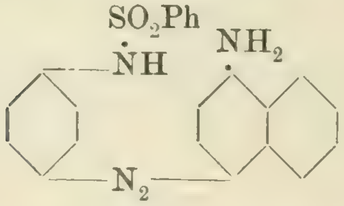
CXLIV.—*The Interactions of Aromatic Amines and para-Diazoimides.*

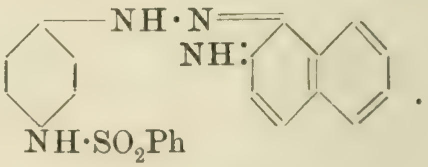
By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

IN this communication the authors call attention to a direct method of producing certain aminoazo-compounds, which, although not generally applicable to all aromatic bases,* is, nevertheless, of some interest, as it consists of a simple additive process occurring between the more reactive amines and the para-diazoimides (Trans., 1905, **87**, 82, 1302). This interaction does not take place with aniline and its homologues and alkyl derivatives, but proceeds quantitatively with the naphthylamines and the more active meta-diamines, such as 2 : 4-tolylenediamine (Trans., 1905, **87**, 1305). The formation of an aminoazo-compound also occurs, although less readily, with the monoalkylnaphthylamines, but this reaction does not take place with the dialkylnaphthylamines. It is therefore very probable that the first step in this additive process consists in the migration of an aminic hydrogen from the base to the diazoimide with the assumption of a quinonoid configuration by the interacting amine:



The resulting compound may subsequently revert to the benzenoid form (I):


(I.)


(II.)

The reaction with β-naphthylamine occurs in a similar manner, only in this case it is the orthoquinonoid configuration (II) which is assumed.

If this explanation of the reaction is correct, it is obvious that the change will occur only when the aminic nitrogen is associated with, at least, one hydrogen atom, and this deduction accords with the fact that no combination takes place between the diazoimides and the dialkylnaphthylamines. In several instances where the interaction could not be effected in this way, it was, nevertheless, brought about by coupling the base, generally a tertiary amine, with the corresponding diazonium salt, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2Cl$, in aqueous solution, provided that sodium acetate or an alkali, or even excess of the base, was added to eliminate the hydrochloric acid set free in the following reaction:

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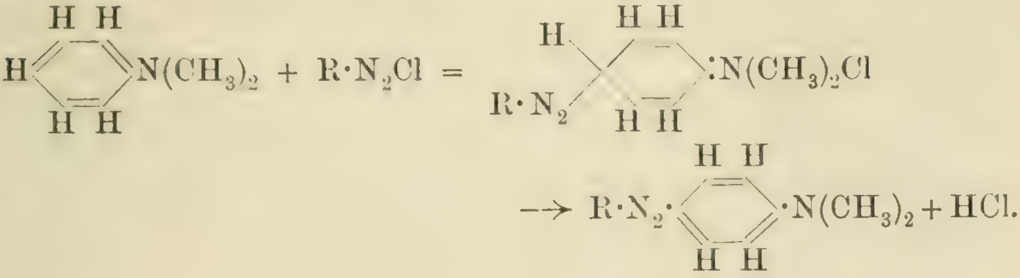
* Meldola and Eynon have summarised the methods generally available for the production of aminoazo-compounds (Trans., 1905, **87**, 1), and it will be seen on reference to this résumé that the changes involved are usually substitutive and not merely additive.



I. *Benzenesulphonyl-*p*-phenylenediazoimide and Benzenoid Amines.*

1. *Aniline.*—Benzenesulphonyl-*p*-phenylenediazoimide and excess of aniline did not interact when warmed at 40—50° for twelve hours, and the former compound crystallised unchanged on cooling the solution. At higher temperatures, the diazoimide decomposed, giving rise to tarry products.

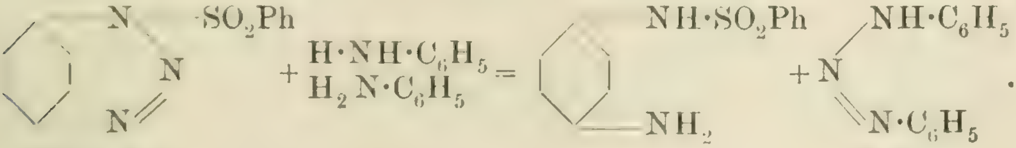
Equal parts by weight of the diazoimide and aniline hydrochloride (3·5 grams of each) were heated in excess of aniline for seven hours at 45°, a small quantity of nitrogen was evolved and the solution darkened. Treatment of the product with dilute hydrochloric acid led to the formation of a dark blue, sparingly soluble hydrochloride, which, after crystallisation from dilute alcoholic hydrochloric acid, separated in steel-blue crystals and was identified as aminoazobenzene hydrochloride:

Cl = 14·87 and 15·09 ; theory requires Cl = 15·01 per cent.

This product weighed 1·5 grams and gave, on treatment with ammonia, aminoazobenzene melting at 122°.

The filtrate from this hydrochloride, when treated with sodium acetate, furnished a pale yellow base, which, after crystallisation from dilute alcohol, was identified as benzenesulphonyl-*p*-phenylenediamine (m. p. 168—170°), the yield of which was 3·3 grams, this being more than 90 per cent. of the calculated amount.

This result shows that the reaction under investigation is an interesting case of the migration of diazo-nitrogen:



In the presence of aniline hydrochloride, the diazoaminobenzene thus produced is chiefly converted into the isomeric aminoazobenzene, whilst a small proportion undergoes a destructive change, evolving nitrogen and giving rise to tarry products.

2. *Methylaniline.*—The diazoimide and redistilled methylaniline did not interact when warmed together for eighteen hours at 45—50°.

The azo-derivative was obtained by dissolving the diazoimide in dilute hydrochloric acid and mixing this solution with methylaniline dissolved in alcohol. A faint red coloration was produced and the addition of sodium acetate induced the gradual deposition of a viscid, orange precipitate. This product when crystallised from alcohol separated in large, yellowish-brown, prismatic crystals and melted at 143°:

0·2482 gave 29·2 c.c. nitrogen at 20° and 762·5 mm. N = 13·50.

$C_{19}H_{18}O_2N_4S,C_2H_5\cdot OH$ requires N = 13·59 per cent.

Another specimen of this compound, after three crystallisations from benzene, separated in ochreous crystals melting at 170°:

0·1420 gave 18·6 c.c. nitrogen at 21° and 761 mm. N = 14·95.

$C_{19}H_{18}O_2N_4S$ requires N = 15·31 per cent.

3. *Dimethylaniline.*—Negative results only were obtained on heating benzenesulphonyl-*p*-phenylenediazoimide with dry dimethylaniline, either alone or in the presence of dimethylaniline hydrochloride. In the former experiment, 90 per cent. of the diazoimide was recovered unchanged, whilst in the latter, nitrogen was evolved and tarry products only were formed.

Benzenesulphonyl-p-*aminobenzeneazodimethylaniline*,

$$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N(CH_3)_2,$$

was produced when benzenesulphonyl-*p*-aminobenzenediazonium chloride, produced either by direct diazotisation or by dissolving the diazoimide in cold hydrochloric acid, was allowed to react with dimethylaniline dissolved in alcohol. Only a faint coloration developed at first, showing that the tendency for the azo-condensation is very slight. The interaction was, however, promoted by adding sodium acetate in insufficient amount to precipitate the diazoimide. The aminoazo-derivative separated in the form of its purple hydrochloride and was set free and crystallised from benzene, when it separated partly in sheaf-like clusters of yellow needles and partly as orange prisms, both forms melting at 182—183°:

0·0596 gave 7·5 c.c. nitrogen at 19° and 762 mm. N = 14·51.

$C_{20}H_{20}O_2N_4S$ requires N = 14·73 per cent.

The two preceding aminoazo-compounds developed brownish-orange colorations with concentrated sulphuric acid.

II. *Benzenesulphonyl*-p-*phenylenediazoimide and Naphthalenoid Amines.*

1. *a-Naphthylamine.*—The interaction of benzenesulphonyl-*p*-phenylenediazoimide and *a*-naphthylamine occurred even on triturating these substances together at the ordinary temperature, the solid mixture immediately developing a red colour. The formation of aminoazo-compound was completed by gently warming the mixture, and the excess of *a*-naphthylamine employed was removed by treatment with dilute hydrochloric acid. The residue, which consisted of the dark purple hydrochloride of the aminoazo-base, was treated with ammonia, and the liberated amine crystallised repeatedly from alcohol, when brownish-orange needles were obtained, melting at 172°; an intense crimson coloration was developed on treating the compound with concentrated sulphuric acid:

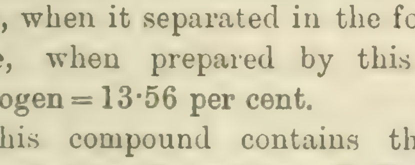
0·2542 gave 20·3 c.c. nitrogen at 18° and 763 mm. N = 13·83.
$C_{22}H_{18}O_2N_4S$ requires N = 13·93 per cent.

Benzenesulphonyl-p-*aminobenzene-4-azo-a-naphthylamine* (formula I) was also readily obtained by coupling *a*-naphthylamine with benzenesulphonyl-*p*-aminobenzenediazonium chloride in dilute alcoholic solution, when it separated in the form of its purple hydrochloride. The base, when prepared by this method, melted at 172° and gave nitrogen = 13·56 per cent.

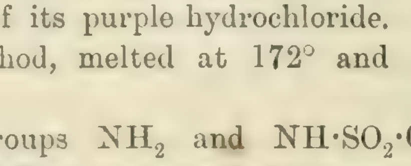
This compound contains the groups NH_2 and $NH\cdot SO_2\cdot C_6H_5$ separated by the residue $-C_6H_4\cdot N_2\cdot C_{10}H_6-$, and an attempt was made to prepare the cyclic diazoimide, $C_6H_5\cdot SO_2\cdot \underline{N\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot N_2}$, corresponding with the quinone, $O\colon C_6H_4\colon N_2\colon C_{10}H_6\colon O$, but diazotisation of the base in glacial acetic acid with amyl nitrite or hydrochloric acid and sodium nitrite was accompanied by an elimination of nitrogen, and the corresponding azo-*a*-naphthol,

$$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH,$$

was produced. This compound gave a dark brown, sparingly soluble sodium derivative, which developed a bluish-purple coloration with concentrated sulphuric acid.



(I.)



(II.)

2. *β-Ethoxy-a-naphthylamine.*—This base reacted with the para-diazoimide quite as readily as *a*-naphthylamine itself, the substances combining even when intimately mixed in cold pyridine solution.

The azo-compound was also readily obtained when the base and the corresponding diazonium chloride were coupled in aqueous solutions.

Benzenesulphonyl-p-*aminobenzene*-4-*azo*-2-*ethoxy*-α-*naphthylamine* (formula II) crystallised from benzene in red, acicular prisms with a green reflex; it melted at 176° and yielded a hydrochloride which separated from its deep purple solution in green crystals melting at 203—204°. The free azo-base furnished the following analytical result:

0·2378 gave 27·1 c.c. nitrogen at 22° and 758 mm. N = 12·87.

$C_{24}H_{22}O_3N_4S$ requires N = 12·55 per cent.

3. *Ethyl-α-naphthylamine.*—This base was prepared by adding slowly 85 grams of ethyl bromide, dissolved in 80 c.c. of alcohol, to a boiling solution of 100 grams of α-naphthylamine in 240 c.c. of the same solvent. A crystalline precipitate of ethyl-α-naphthylamine hydrobromide was slowly produced, and this salt when treated with either potassium hydroxide or potassium carbonate yielded ethyl-α-naphthylamine, an oily base which was extracted with ether and subsequently dried and fractionated. This amine boiled at 325—330°/776 mm., and when rectified under diminished pressure it boiled at 191°/16 mm., and was then obtained colourless, although on exposure to the atmosphere it darkened and became dichroic, being brown by transmitted and violet by reflected light.

The ease with which this base can be obtained from its hydrobromide by the action of alkali hydroxides does not bear out the statement that this salt on treatment with potassium hydroxide yields α-naphthylamine and not ethyl-α-naphthylamine (Limpricht, *Annalen*, 1856, **99**, 117; Schiff, *ibid.*, 1857, **101**, 90). When treated with sodium nitrite and hydrochloric acid, this base gives rise to nitrosoethyl-α-naphthylamine (compare Koch, *Annalen*, 1888, **243**, 310).

Ethyl-α-naphthylamine was also prepared by ethylating benzenesulphonyl-α-naphthylamine and then hydrolysing the benzenesulphonylethyl-α-naphthylamine with alcoholic hydrochloric acid in sealed tubes at 135°. The foregoing method is, however, much more convenient, and yields ethyl-α-naphthylamine containing only a trace of unaltered α-naphthylamine.

Benzenesulphonylethyl-α-*naphthylamine*, $C_6H_5\cdot SO_2\cdot N(C_2H_5)\cdot C_{10}H_7$, crystallised from alcohol in colourless prisms which acquired a mauve tint; it melted at 112—113°:

0·5852 gave 0·4442 $BaSO_4$. S = 10·42.

$C_{18}H_{17}O_2NS$ requires S = 10·28 per cent.

Ethyl-α-naphthylamine and benzenesulphonyl-*p*-phenylenediazoimide interacted when warmed together in pyridine for five hours at 50°, although the combination did not occur so readily when the reagents were mixed in the absence of this medium. The aminoazo-compound when crystallised from alcohol separated in dark red, prismatic crystals and melted at 177—179°.

*Benzenesulphonyl-*p*-aminobenzene-4-azoethyl-α-naphthylamine.*—Ethyl-α-naphthylamine and benzenesulphonyl-*p*-aminobenzenediazonium chloride interacted very readily in aqueous solution; the hydrochloride of the aminoazo-compound being deposited as a bulky, dark purple precipitate, from which the base was obtained by the action of ammonia.

This preparation, when recrystallised from alcohol, gave transparent, crimson, lath-like crystals, which melted at 179° and did not depress the melting point of the substance prepared from ethyl-α-naphthylamine and the diazoimide:

0·1926 gave 23·3 c.c. nitrogen at 22° and 758 mm. N = 13·67.
$C_{24}H_{22}O_2N_4S$ requires N = 13·04 per cent.

4. *Dimethyl-α-naphthylamine.*—A sample of this base, prepared by Hantzsch's method (*Ber.*, 1880, **13**, 1348; 1888, **21**, 3124), was redistilled from acetic anhydride to remove any primary or secondary amine and then, finally, rectified under the ordinary pressure. When the base was heated for several hours with benzenesulphonyl-*p*-phenylenediazoimide at 50°, no combination occurred, and the greater portion of the diazoimide was recovered unchanged. Dimethyl-α-naphthylamine was then coupled with benzenesulphonyl-*p*-aminobenzenediazonium chloride in the manner indicated in the case of dimethylaniline. The dark green hydrochloride of *benzenesulphonyl-*p*-aminobenzene-4 azodimethyl-α-naphthylamine*,

$$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot N(CH_3)_2,$$

was deposited very slowly, and the reaction was completed only after several days, sodium acetate being slowly added in small quantities. The free aminoazo base was crystallised either from glacial acetic acid or from a mixture of benzene and light petroleum (b. p. 80—100°); from the former medium, it separated in dark garnet-red crystals having a green reflex, whilst from the latter it was deposited in red, nodular prisms; both forms melted at 155—156°:

0·1972 gave 23·0 c.c. at 21° and 774 mm. N = 13·53.
$C_{24}H_{22}O_2N_4S$ requires N = 13·04 per cent.

The two preceding aminoazo-compounds developed a crimson coloration with concentrated sulphuric acid.

5. *β-Naphthylamine.*—The para-diazoimide and β-naphthylamine combined readily when intimately mixed and slightly warmed, the reaction being accelerated by the addition of a small amount of pyridine. The mixture was extracted with dilute hydrochloric acid,

the residual hydrochloride decomposed by ammonia, and the aminoazo-compound then crystallised from alcohol.

Benzenesulphonyl-p-*aminobenzeneazo-β-naphthylamine* separated in minute, reddish-brown prisms, melted at 211—212°, and developed a deep bluish-purple coloration with concentrated sulphuric acid:

0·1910 gave 23·3 c.c. nitrogen at 20° and 760 mm. N = 13·95.

$C_{22}H_{18}O_2N_4S$ requires N = 13·92 per cent.

The yield of this base by the foregoing method was practically quantitative.

6. *Ethyl-β-naphthylamine.*—This base and the para-diazoimide did not interact in the cold, but on warming them together with some anhydrous pyridine at 60° for about twelve hours, the colour of the solution deepened and a formation of aminoazo-compound occurred. This substance was, however, contaminated with tarry products and was purified only with great difficulty. After repeated washing with dilute hydrochloric acid and treatment with ammonia, the residue was recrystallised from alcohol until, finally, a small amount of the aminoazo-base was obtained, which melted at 172° and did not depress the melting point of the compound prepared by coupling ethyl-*β*-naphthylamine and benzenesulphonyl-*p*-aminobenzenediazonium chloride in dilute alcohol.

Benzenesulphonyl-p-*aminobenzeneazoethyl-β-naphthylamine*,

$$C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_2H_5,$$

when prepared by the latter method separated at once as a red precipitate, which, when recrystallised from alcohol, furnished bright scarlet leaflets melting at 176°:

0·1466 gave 17 c.c. nitrogen at 21° and 773 mm. N = 13·42.

0·3960 ,, 0·2282 $BaSO_4$. S = 7·91.

$C_{24}H_{22}O_2N_4S$ requires N = 13·04; S = 7·44 per cent.

Both preparations gave an intense greenish-blue coloration with concentrated sulphuric acid.

7. *Dimethyl-β-naphthylamine.*—This tertiary base showed no tendency either to combine additively with benzenesulphonyl-*p*-phenylenediazoimide, or to couple with benzenesulphonyl-*p*-aminobenzenediazonium chloride in dilute alcoholic solution.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

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CXLV.—*Succinic Acid and its Potassium Salts.*

By Hugh Marshall and Alexander Thomas Cameron.

In a paper recently published by one of us (Cameron, "Variations in the Crystallisation of Potassium Hydrogen Succinate due to the presence of other Metallic Compounds in the Solution," *Proc. Roy. Soc. Edin.*, 1905, **25**, 449) attention was called to the formation of crystals of potassium hydrogen succinate bounded entirely by curved faces, from solutions containing chromic, ferric, and other compounds. As the subject is one of considerable crystallographic interest, it was decided to carry out a fuller investigation in order to discover, if possible, the exact conditions which induce the phenomenon. It at once became evident, however, that before this problem could be attacked it would be necessary to investigate some points connected with the various potassium succinates themselves, since the published data concerning them proved to be in several important respects erroneous, and even at variance with one another.

The experiments undertaken for this purpose have given results which in certain respects are novel and of considerable interest; so much so that it appears desirable to undertake a thorough investigation of the whole question of the formation of the acid succinates of the alkali metals generally, probably also that of the acid salts of other members of the oxalic acid series. As such an investigation will take some time, however, it is considered advisable to publish now the preliminary results obtained with the potassium salts, which have cleared the ground sufficiently for the purposes of the investigation originally contemplated—that concerning the formation of crystals with curved boundaries.

The published data regarding the succinates are derived mostly from papers by Doepping (*Annalen*, 1843, **47**, 253) and Fehling (*ibid.*, 1844, **49**, 155). These papers deal with the succinates in general; the authors' statements regarding the potassium salts may be summarised as follows:

Normal potassium succinate is obtained, according to Doepping, by neutralising succinic acid with potassium carbonate, and allowing the solution to crystallise. It forms indeterminate crystals, the composition of which corresponds to the formula $K_2C_4H_4O_4,2H_2O$;[*] it is soluble in spirits of wine, insoluble in ether; it effloresces in the air and is completely dehydrated at 100°. Fehling states that he obtained this salt, by a method similar to the above, in thin rhombic tables resembling those of potassium chlorate; it is soluble in water, and in not too strong spirit, and is stable in the air. Further, from the mother liquor another salt separated in less distinct crystals, which abstracted moisture from the air but did not deliquesce even after a prolonged time. The analysis of the first crystals gave results leading to the formula $K_2C_4H_4O_4,\frac{1}{2}H_2O$; the composition of the second crystals obtained from the mother liquor is not stated. According to a more recent investigation by Salzer (*Ber.*, 1883, **16**, 3025) the salt forms very deliquescent rhombic crystals, the composition of which corresponds to the formula $K_2C_4H_4O_4,3H_2O$.

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[*] All formulæ here given are translated into modern notation where necessary.

Acid potassium succinate is obtained, according to Doepping, by taking two equal portions of acid, saturating one with potassium succinate, and then adding the other portion to the neutral solution; on evaporation, six-sided prisms separate, belonging to the rhombic system and having the composition represented by the formula $KHC_4H_4O_4,2H_2O$. They effloresce on exposure to the air and lose all water at 100°; they are easily soluble in spirit and in water. Fehling gives no particulars regarding the preparation of this salt but merely states that the air-dried salt is anhydrous and gives analytical results agreeing with the formula $KHC_4H_4O_4$.

Superacid potassium succinate was obtained, according to Fehling, by dissolving the preceding compound in just as much acid as it already contained, and allowing the warm solution to cool. Analysis gave results agreeing with a formula $KH_3(C_4H_4O_4)_2,H_2O$, but on drying at 100° there was a loss of water equivalent to $1\frac{1}{2}H_2O$, and Fehling therefore assumes for the anhydrous salt a formula the modern equivalent of which would be $K_2H_4(C_4H_4O_4),C_4H_4O_3$; he adds that this (constitutional) dehydration was not due to the drying at 100°, since he subsequently obtained this same anhydrous salt by direct crystallisation from solution. Doepping makes no mention of any superacid salt. Salzer (*loc. cit.*) obtained a salt $KH_3(C_4H_4O_4)_2$ when trying to prepare the acid salt, and concluded that he had taken an insufficient proportion of potassium carbonate; in a subsequent experiment he obtained the hydrated acid salt described by Doepping.

It is interesting to note that Fehling, in the introduction to his paper, calls particular attention to the discrepancies between his results and those of Doepping, and makes the somewhat remarkable statement: "I must admit that these various differences in the salts prepared by us did not surprise me, for, in the course of my work, I had often had the experience that, under apparently completely similar conditions, salts of different composition were formed—an experience which cost me much time and trouble before I convinced myself of its correctness. This cause contributed greatly to the delay [in publication], since I at first ascribed to foreign substances the differences in the composition of salts which had been prepared in the same way.

Only repeated investigation of the acid, and ultimate analysis of the compounds, have convinced me of the fact that under apparently similar conditions the succinates form different compounds with water —different both as regards the proportion of water taken up and the temperature at which this water is lost. I have sought to explain, why at one time the one salt should be formed and at another time one of different composition, partly by different concentration of the solution, partly by difference of temperature, and also, more particularly by the fact that crystallised acid or anhydrous acid was used for that particular preparation, but I have been unable to make out the cause with certainty; nor have I been able to prepare at pleasure the one salt or the other. It is therefore very probable that, on repetition of the experiments, salts will be found which differ in composition from those investigated by Mr. Doepping or myself."

The results given in the present paper clear up the difficulties regarding the potassium salts, and render advisable a fuller investigation of the other salts in the light of modern knowledge.

When we first sought to prepare the two acid potassium succinates we acted on the statements made by Doepping and Fehling, weighing out calculated quantities of pure succinic acid (Merck) and potassium carbonate, such that when their solutions were mixed the resulting solution should contain potassium and acid-hydrogen in the ratio K : 3H in one case and K : H in the other; the slightly warm solutions were then set aside to crystallise. In neither case was the expected result obtained: the more acid solution gave a fairly abundant crop of pure succinic acid, whilst the other gave crystals of what proved to be the anhydrous superacid salt $KH_3(C_4H_4O_4)_2$. Assuming that no error had been made in the proportions taken in each case, this indicated that the acid salts separate only from solutions containing a higher ratio of K to H than that which is present in the salts themselves. That this was correct in one case at least was easily proved by dissolving the crystals of superacid salt in water and allowing the solution to evaporate spontaneously: succinic acid crystallised out at first. Confirmation was obtained on analysing the mother liquors; that which had yielded superacid salt had the K : H ratio greater that 1 : 1; that which had yielded free acid had the ratio greater than 1 : 3. The solution prepared from the superacid salt was allowed to go on evaporating, the crystals being removed from time to time. After a fair quantity of free acid had crystallised, crystals of superacid salt were next obtained; these in turn gave place to the hydrated acid salt; and this again to anhydrous acid salt. No other salt was obtained by spontaneous evaporation. A solution prepared from pure crystals of acid salt gave superacid salt as a first product, as expected from the previous observations.

In each case, when a solution was prepared from crystals of one of the salts, if the crystals first formed were allowed to remain in the solution they began to disappear again as soon as the second salt made its appearance, so that ultimately the salt originally taken was alone obtained by slow evaporation to dryness.

From these results, therefore, it is evident that the two acid potassium succinates behave at the ordinary temperature like two double salts which are within their "transition intervals," and cannot exist in equilibrium with a solution containing the two components in the ratio in which they are present in the crystals. It was therefore necessary to obtain a series of determinations of the "simultaneous solubilities" of potassium succinate and succinic acid under various conditions, and so establish the limits of concentration determining the formation of the various salts.

In addition to the salts already mentioned, which for the sake of brevity may be designated by the formulæ KH_3Su_2, KHSu, and

$$KHSu,2H_2O,$$

the only other crystallised salt which we have been able to prepare is the normal salt, which corresponds to the formula $K_2Su,3H_2O$, as stated by Salzer. Crystallographic descriptions of the acid salts will be given later, as these do not appear to have been previously published, but a few details of other properties may be given here.

The physical properties of succinic acid itself have been somewhat fully studied by previous investigators. We have confirmed the melting point 181° (uncorr.), the figure given in the majority of cases (Davidoff, *Ber.*, 1886, **19**, 407, gives the corrected value 185°). The density has been determined by Bodeker (*Jahresber.*, 1860, 17), who gives the value 1·552; also by Tanatar and Tschelebieff (*J. Russ. Phys. Chem. Soc.*, 1892, **22**, 548), who give 1·554. Using Retgers' method, with bromoform and turpentine, we obtained the value 1·562. The solubility of the acid in water has been determined by Bourgoin (*Bull. Soc. chim.*, 1874, **21**, 110) and by Miczynski (*Monatsh.*, 1886, **7**, 265); a comparison of their results with those which we have ourselves obtained is given in the following table, where the solubility is expressed in terms of grams of acid per 100 grams of solvent.

Solubility of Succinic Acid in Water.

	Bourgoin.	Miczynski.	M. and C.
0·0°	2·88	2·804	2·77
14·5	5·14	—	—
20·0	—	6·893	6·84
25·0	—	—	8·59
27·0	8·44	—	—
40·0	—	16·214	14·86
40·5	15·37	—	—

The superacid salt crystallises as well-formed prisms or plates, with bright lustrous faces, permanent in air. The crystals are rapidly decomposed by absolute alcohol; succinic acid goes into solution and a powder of the monoacid salt remains. The density, determined by Retgers' method in a mixture of bromoform and turpentine, is 1·559. When heated, the crystals fuse to a clear liquid, and exhibit a sharp melting point at 162°. On further heating, the liquid decomposes with evolution of acid vapours, forming a charred mass. The crystals themselves are very soft and can be easily crumbled between the fingers.

The monoacid salt crystallises at moderately low temperatures in the form of the dihydrate, in transparent prisms or tables. These rapidly effloresce on exposure to air, but retain their shape. From slightly warm solutions, or from solutions containing much normal salt, anhydrous crystals are obtained. These separate as prisms or as flat tabular crystals with rhombic outline, or as thin brittle sheets united in clusters or rosettes. The salt is practically insoluble in absolute alcohol, but is slightly soluble in alcohol mixed with water, from which it separates in the anhydrous form. It melts at 240–2°, with indications of decomposition. The density of the hydrate is about 1·616, that of the anhydrous crystals is 1·767.

The conditions for obtaining the one or the other acid salt will appear from the solubility curves. The salts cannot of course be recrystallised from pure aqueous solution at the ordinary temperature; the anhydrous salt can be recrystallised from dilute alcohol, or may be reprecipitated from the aqueous solution by adding alcohol to it, or placing it in a desiccator over alcohol; in the latter case it deposits in crystals which are often very irregularly grown.

The normal salt may be obtained by mixing solutions of the calculated quantities of pure succinic acid and potassium carbonate, boiling the solution to expel all carbon dioxide, evaporating to small bulk, and allowing to crystallise. The salt can be purified by recrystallisation from water, in which it is very soluble. As it is obtainable commercially, this material may be used, after recrystallising. In preparing the salt from the acid satisfactory results cannot easily be obtained by using indicators, as in concentrated solutions there is no definite neutralisation point with, say, litmus, especially when carbonate is used. If a concentrated solution of pure normal salt is allowed to stand exposed to the air it absorbs carbon dioxide and gradually deposits scales of anhydrous potassium hydrogen succinate. This is brought about fairly rapidly if a stream of carbon dioxide is passed through the solution; doubtless, bicarbonate is simultaneously formed to a considerable extent and remains dissolved:

$$K_2C_4H_4O_4 + H_2O + CO_2 \rightleftharpoons KHC_4H_4O_4 + KHCO_3.$$

If the solution is boiled, there is a very brisk evolution of carbon dioxide, far greater than would be expected if there were no considerable storage of it in the form of bicarbonate. The separation of acid salt here referred to doubtless explains some of the discrepancies in the description of the properties of the crystals of the normal salts given by earlier observers.

When alcohol is added to a moderately concentrated solution of the normal salt two liquid layers separate, and only by repeated treatment with fresh alcohol does a crystal mass form from the dense aqueous layer. By continuing the treatment with absolute alcohol the crystals become converted into a white powder, owing to dehydration; the salt dissolves in the alcohol to only a very slight extent. Although the crystals deliquesce in the air, they slowly effloresce over sulphuric acid. Contrary to what is stated by Salzer, the salt can be completely dehydrated by heating to 100°, though somewhat slowly. The density of the hydrate is about 1·564.

As it was evident from the rapid efflorescence of the hydrated acid salt that its transition temperature into the anhydrous form lies little above the ordinary temperature, this point was determined dilatometrically before proceeding with the solubility determinations. Since the dilatometer was charged with the pure salt very slightly moistened, the determination gives, of course, the triple point at which $KHSu,2H_2O$, $KHSu$, and KH_3Su_2, are in equilibrium with solution. This point was found to be 22·5°.

Another dilatometer was charged with $KHSu,2H_2O$ mixed with $K_2Su,3H_2O$, and moistened, and the other triple point determined. This was found to be 14°.

On cooling the mixtures in the dilatometers there were slight indications of other changes at 3° in the first and 5° in the second. This may be due to the formation of a higher hydrate, but so far no such compound has been isolated.

When tested in the dilatometer no change was found in the case of the normal salt up to 80°; nor in the case of the superacid salt up to 50°, either alone or in contact with succinic acid or the monoacid salt.

The first series of solubility determinations was performed at 25°, so as to obtain an isotherm free from the complication due to the existence of hydrated as well as anhydrous acid salt. The materials were placed in glass tubes fitted with rubber stoppers, and rotated for several hours in a thermostat. Suitable quantities of solution (usually about 2 c.c.) were then withdrawn by means of a pipette through caps of filter paper, transferred to flat glass dishes fitted with ground stoppers, and weighed. To determine the amount of succinic acid and of potassium succinate, the solution was evaporated to constant weight in a water-oven, whereby the combined weight of the two ingredients was obtained; the residue was then dissolved in water and the acid determined by titration with standard baryta solution, using phenolphthalein as indicator. There is a risk of loss of succinic acid if the evaporation is forced too rapidly, especially with solutions containing excess of acid. In the case of solutions saturated in contact with the free acid, this was avoided by preparing solutions containing known concentrations of potassium succinate and agitating them with crystals of the acid; in these cases all that was necessary was to titrate a weighed quantity of the solution. Deducting the weight of acid found, the weight of water and potassium succinate was obtained, and the ratio of these to each other was known.

Determination of the potassium as sulphate was tried but did not work so well, owing to the charring and considerable evolution of gas on heating with sulphuric acid. In a few cases the solution was first titrated and then evaporated to dryness, the weight of barium succinate being then deducted from the weight of residue; but this method did not prove so satisfactory as the other.

Determinations were also carried out at 0°, 20°, and 40°, but not on so extensive a scale. The method adopted was similar, except that at 0° the solution was placed in an open tube embedded in a mixture of water and finely-powdered ice, and was stirred by means of a vertical rotating stirrer.

In many instances duplicate determinations were made, especially at the double points. Considerable difficulty was experienced in definitely locating the double points between normal salt and acid salt; as we were not particularly concerned about this region only a few experiments were devoted to it, and they are less trustworthy than the others. Very erratic results were at first obtained for the solubility of the normal salt itself; this appears to have been due to the difficulty of avoiding the presence of either acid salt or carbonate. The results have been calculated in all cases to mols. of K_2Su and H_2Su per 100 mols. H_2O, as given in the following table; they have also been plotted in the form of a diagram, which can be much more easily followed (see p. 1528).

Table I.

Analysis of Saturated Aqueous Solutions of the Potassium Succinates.

No. of expt.	Weight of solution.	Weight of solid.	Succinic acid, determined by titration.	Potassium succinate, by difference.	Mols. $H_2C_4H_4O_4$.	Mols. $K_2C_4H_4O_4$.	
Temperature 0°.							
1.	1·8374	—	0·0493	—	0·421	—	
2.	1·7915	—	0·0489	—	0·424	—	
3.	2·0357	0·3125	0·1477	0·1648	1·309	0·887	double point
4.	0·6943	0·1078	0·0546	0·0532	1·422	0·840	
5.	2·1493	0·3910	0·1771	0·2139	1·537	1·128	
6.	1·2031	0·2512	0·0975	0·1537	1·563	1·496	
7.	0·7120	0·1662	0·0548	0·1114	1·533	1·891	double point
8.	1·9437	0·4540	0·1532	0·3008	1·569	1·872	
9.	1·2189	0·4899	—	—	—	6·230	
Temperature 14°. Solution in equilibrium with $K_2Su,3H_2O$, $KHSu,2H_2O$ and KHSu.							
10.	1·5671	0·6967 $\left\{\begin{matrix}BaSu\\K_2Su\end{matrix}\right\}$	0·0230	0·6474	0·391	6·691	
Temperature 15·9°. Solution in equilibrium with $KHSu,2H_2O$ and KHSu.							
11.	2·4796	0·8941	0·0421	0·8520	0·405	4·982	
Temperature 20°.							
12.	2·0519	—	0·1311	—	1·042	—	
13.	2·0439	—	0·1310	—	1·045	—	
14.	2·0779	—	0·1617	[2·025%]	1·314	0·188	
15.	1·6332	0·1507	0·1205	0·0302	1·240	0·189	
16.	1·9910	0·3598	0·2216	0·1682	2·074	0·785	
17.	2·1619	—	0·2465	[8·400%]	2·129	0·779	
18.	2·2432	0·5903	0·3287	0·2616	3·034	1·467	
19.	2·2258	—	0·3254	[15·403%]	3·015	1·428	
20.	1·6357	0·4654	0·2433	0·2221	3·173	1·760	double point
21.	2·0895	0·5923	0·3140	0·2783	3·201	1·724	
22.	2·2479	0·6414	0·3417	0·2997	3·244	1·730	
23.	2·2867	0·6717	0·3433	0·3284	3·244	1·884	
24.	2·3244	0·7387	0·3097	0·4290	2·980	2·508	
25.	2·3839	0·8395	0·3038	0·5357	3·004	3·218	double point
26.	2·3710	0·8296	0·2938	0·5358	2·909	3·223	
27.	2·3882	0·8269	0·2795	0·5474	2·732	3·250	
28.	2·5859	1·1325	0·0443	1·0882	0·465	6·941	
29.	2·6294	1·2721	0·0276	1·2445	0·310	8·500	double point
30.	2·6912	1·3208	0·0265	1·2943	0·295	8·755	
31.	2·6622	1·3215	0·0242	1·2973	0·276	8·970	
32.	1·8270	1·0000	0·0029	0·9971	0·053	11·177	
33.	2·2029	1·2468	—	—	—	12·089	
Temperature 25°.							
34.	2·0538	—	0·1620	—	1·307	—	
35.	2·0569	—	0·1634	—	1·317	—	
36.	2·0877	—	0·1912	[2·025%]	1·570	0·188	
37.	2·1086	0·2768	0·2100	0·0668	1·749	0·338	
38.	2·1041	0·2757	0·2101	0·0656	1·754	0·333	

TABLE I (*continued*).

Analysis of Saturated Aqueous Solutions of the Potassium Succinates.

Temperature 25°.

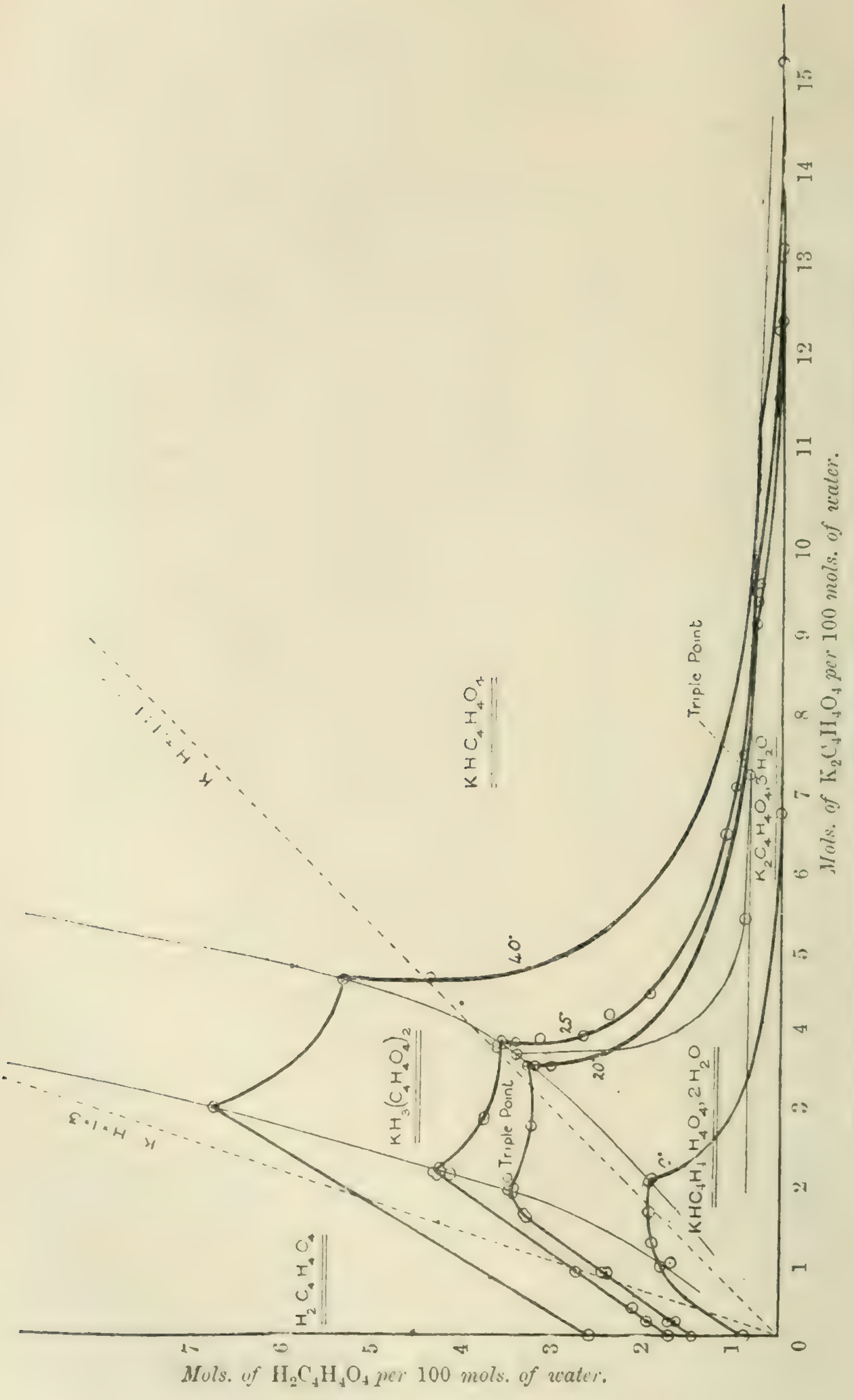
No. of expt.	Weight of solution.	Weight of solid.	Succinic acid, determined by titration.	Potassium succinate, by difference.	Mols. $H_2C_4H_4O_4$.	Mols. $K_2C_4H_4O_4$.	
39.	2·1827	—	0·2790	[8·400%]	2·424	0·779	
40.	2·2824	0·7245	0·4016	0·3229	3·934	1·921	
41.	2·2869	0·7458	0·4128	0·3330	4·088	2·003	double point
42.	2·2738	0·7345	0·4091	0·3254	4·056	1·960	
43.	2·2997	0·7477	0·4189	0·3288	4·119	1·964	
44.	2·2400	0·7232	0·4070	0·3162	4·095	1·933	
45.	2·3443	0·7947	0·3572	0·4375	3·520	2·610	
46.	2·3445	0·7939	0·3606	0·4333	3·549	2·591	
47.	2·4010	0·8999	0·3343	0·5656	3·392	3·486	double point
48.	2·3852	0·8886	0·3266	0·5620	3·330	3·481	
49.	2·3756	0·8845	0·3306	0·5539	3·383	3·444	
50.	2·3983	0·8969	0·3264	0·5705	3·318	3·523	
51.	2·3395	0·8690	0·3159	0·5531	3·279	3·487	
52.	2·3806	0·8783	0·3110	0·5673	3·160	3·501	
53.	2·4006	0·8742	0·2878	0·5864	2·877	3·562	
54.	2·4114	0·8465	0·2406	0·6059	2·347	3·590	
55.	2·4699	0·8727	0·2136	0·6591	2·040	3·826	
56.	2·4319	0·8565	0·1607	0·6958	1·557	4·095	
57.	2·5000	1·0205	0·0650	0·9555	0·671	5·987	
58.	2·5350	1·0825	0·0533	1·0292	0·560	6·569	
59.	1·3842	0·6882	0·0142	0·6740	0·315	8·981	double point
60.	0·6942	0·3918	0·0009	0.3909	0·045	11·983	
61.	0·7871	0·4579	—		—	12·897	
62.	2·2898	1·3338	—	—	—	12·936	
63.	2·7743	1·6124	—	—	—	12·866	

Temperature 40°.

No. of expt.	Weight of solution.	Weight of solid.	Succinic acid, determined by titration.	Potassium succinate, by difference.	Mols. $H_2C_4H_4O_4$.	Mols. $K_2C_4H_4O_4$.	
64.	1·0566	—	0·1369	—	2·272	—	
65.	0·5420	—	0·0702	—	2·271	—	
66.	2·1666	—	0·2795	—	2·260	—	
67.	2·4485	1·0380	0·6240	0·4140	6·751	2·721	double point
68.	2·3440	1·0423	0·4458	0·5965	5·227	4·218	double point
69.	1·2851	0·5447	0·2033	0·3414	4·191	4·275	
70.	2·7266	1·6924	—	—	—	15·170	

Examination of the diagram shows that at 40° the monoacid salt is no longer within its transformation interval, so that above 30—35° it can be recrystallised without decomposition. This is still not the case with the superacid salt, but there are indications that it also is tending in the same direction. This was confirmed by the following experiment. A quantity of superacid salt was completely dissolved in the minimum quantity of hot water and left for some time in a water-oven at about 80°. It was then sown with some small crystals of

FIG 1.



The isotherms are represented by thick lines, the thin lines separate the different systems.

succinic acid; these gradually dissolved. It was next sown with crystals of superacid salt; these grew in the solution. The temperature mentioned would therefore appear to be above the transformation interval for this salt.

The greatest interest of the diagram, however, is provided by those parts of the isotherms relating to the solid succinic acid phase. In the first place these show that the solubility of succinic acid in solutions of potassium succinate is much greater than in water only. One result of this is the apparent paradox that if a solution containing, say, 0·5 molecule of K_2Su, and 2 molecules of H_2Su per 100 molecules of water, is allowed to evaporate at 25°, it will deposit succinic acid, but at the same time become more and more acid itself, reaching a maximum of about 4 molecules of H_2Su to 2 of K_2Su, and 100 of water.

This increased solubility of succinic acid in solutions of its potassium salt is not in itself surprising. Succinic acid is a somewhat weak dibasic acid, and the addition of potassium succinate to its solution should produce an effect more or less approximating to that shown by the equation:

$$H_2C_4H_4O_4 + K_2C_4H_4O_4 = 2K^{\cdot} + 2HC_4H_4O_4'.$$

Since succinic acid gives relatively few $HC_4H_4O_4'$ ions, we might therefore expect it to dissolve in the highly-ionised acid-salt solution to almost, but not quite, as great an extent as in water alone; in other words, the addition of 1 molecule of K_2Su to a solution in contact with solid acid might cause the dissolution of nearly 1 additional molecule of H_2Su.

If the isotherms for the solid succinic acid phase are examined, however, it is found that they rise at a considerably steeper angle than 45°, showing that the addition of 1 molecule of K_2Su leads to the dissolution of considerably more than 1 molecule of additional H_2Su. Further, as appears from the diagram, the steepness increases with rise of temperature, so that the effect is more pronounced at higher temperatures. Taking the solubilities of succinic acid alone at the four temperatures examined:

0°	20°	25°	40°
0·422	1·043	1·312	2·268

deducting them from the maximum solubilities in presence of potassium succinate (first double points):

1·365	3·206	4·089	6·751

we obtain, as respective increases:

0·943	2·163	2·777	4·483

and dividing these by the amounts of potassium succinate in solution at the double points:

0·863	1·738	1·865	2·721

we obtain for the ratio, *extra* $H_2Su : K_2Su$, the values:

1·09	1·24	1·41	1·65

From these ratios, it is very evident that the increase in the amounts of succinic acid dissolved cannot be explained merely on the assumption of the formation of $HC_4H_4O_4'$ ions; we must assume the formation of a more complex ion in considerable quantity, the proportion of this ion being much greater at higher temperatures. The simplest assumption is, of course, that of an ion $C_8H_{11}O_8'$ formed from a disuccinic acid. The "superacid salt" would, in that case, not be really a succinate at all, but might be the normal or an acid salt of the polymerised acid.

A certain amount of confirmation for the view that the superacid salt is not merely a "molecular compound" of KHSu and H_2Su is provided by a comparison of the densities of the acid and the salts. As we have already stated, the density of succinic acid is 1·562, that of the superacid salt is 1·559, and that of the anhydrous acid salt 1·767. As a general rule the density of a double salt is greater than the mean density of its components (compare dolomite, sodium potassium sulphate), but here the density of the intermediate salt is not only less than the mean, but less than that of each component—less than that of succinic acid itself.

The melting point is considerably less than that of either component: $H_2Su = 181°$; $KH_3Su_2 = 162°$; $KHSu = 240—242°$; but such is also the case with double salts like potassium sodium sulphate. We tried the effect of the addition of succinic acid and of acid salt to the superacid salt, and found that the melting point was very considerably lowered by the former—from 162° to 148°, but that the latter had very little effect, lowering it little more than one degree; it is, of course, possible that KHSu is very sparingly soluble in fused KH_3Su_2.

Previous to the solubility determinations at the two extreme temperatures being carried out, several cryoscopic experiments were tried with various solutions, but these gave no very decisive indications. It is now evident, however, that it would be better to use methods applicable at higher temperatures, and we propose to do this in connexion with future work.

It is at present needless to speculate as to the question whether or not succinic acid itself is to any extent polymerised in aqueous solution, or whether a complex is formed only in the case of the salts.

It is proposed to examine the salts of the other alkali metals, and also to work at higher temperatures.

With regard to the polymerisation of the acid, it may be pointed out that d'Arcet (*Ann. Chim. Phys.*, 1832, [ii], **58**, 282) states that by sublimation he obtained a compound, $C_8H_{10}O_7$, supposed to be a semi-anhydride. Much later, Ramsay and Young (*Phil. Trans.*, 1886, **177**, i, 103), in order to explain a peculiarity in the dissociation curve of succinic acid, refer to the possibility of the formation of a compound having this composition. Such a compound might be either an "anhydro-succinic acid" (on the analogy of the anhydrosulphates, or pyrosulphates) or the anhydride of a polymerised acid.

Crystallography.

The various acid salts do not appear to have been previously described crystallographically. The acid itself has been several times examined; the most trustworthy description is that given by Wyrouboff (*Bull. Soc. franç. Min.*, 1893, **16**, 35), who makes it out to be monoclinic prismatic with the constants:

$$B = 91°20', a : b : c = 0·5688 : 1 : 0·6195.$$

The normal salt has been described by Haushofer (*Zeitsch. Kryst. Min.*, 1884, **9**, 525), who examined Salzer's preparation; he describes it as rhombic bi-pyramidal with the constants:

$$a : b : c = 0·5399 : 1 : 0·9618.$$

Hydrated Potassium Hydrogen Succinate, $KHC_4H_4O_4,2H_2O$.

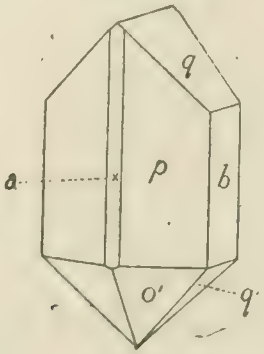
Crystal class.—Rhombic pyramidal:

$$a : b : c = 0·5022 : 1 : 1·0161.$$

Forms observed.—$a = \{100\}$, $b = \{010\}$, $p = \{110\}$, $q = \{011\}$, $q' = \{01\bar{1}\}$ $o' = \{11\bar{2}\}$.

Cleavage.—Perfect on $\{110\}$.

FIG. 2.



Angles.

Angle.	*n.*	Measured.	Average.	Calculated.
010 : 110	20	63°12′—63°33	63°20′*	—
010 : 101	21	44 19 —44 43	44 32·5*	—
112 : $11\bar{2}$	—	—	—	84° 6′
$11\bar{2}$: 010	6	70 18 —70 30	70 23	70 21
112 : 110	3	41 15 —41 37	41 25	41 27
110 : 011	—	—	—	71 21
$01\bar{1}$: $11\bar{2}$	—	—	—	45 15

Very few angles were measured, owing to the very rapid efflorescence of the crystals. In addition to the forms mentioned above, there were observed on a single large crystal faces which evidently belonged to the upper pyramid {112}; this crystal had grown in a solution which contained a considerable proportion of normal salt, since crystals of the anhydrous acid salt had begun to form, notwithstanding a fairly low temperature.

The crystals are, as a rule, either prismatic along the axis of symmetry or tabular on {010}. The pinacoid {100} is rarely well developed, being striated vertically, when present, as if formed by oscillation of the prism form. On large crystals the upper horizontal edge was not sharp, but rounded off, and frequently this end of the crystal was more or less saddle-shaped. On some tabular crystals, growth along the axis of symmetry seemed to be decidedly more rapid in the negative direction than in the positive. Opaque effloresced crystals retain their original shape.

The optic axes lie in the horizontal plane, a being the acute bisectrix, one axis being visible emerging obliquely through the prism. Exact optical determinations could not be made, owing to the rapid efflorescence, but approximate determinations of the refractive indices for the yellow part of the spectrum were obtained by means of a cleavage prism (β and γ) and a natural prism formed by 010 and $0\bar{1}1$ (α):

$$\alpha = 1{\cdot}417\ ;\ \beta = 1{\cdot}5295\ ;\ \gamma = 1{\cdot}533.$$

Anhydrous Potassium Hydrogen Succinate, $KHC_4H_4O_4$.

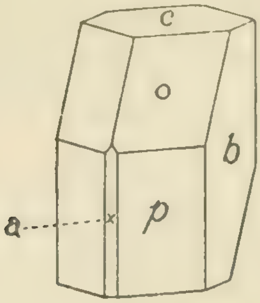
Crystal class: Monoclinic prismatic.

$$\beta = 91°48'.$$

$$a : b : c = 1{\cdot}0081 : 1 : 1{\cdot}3102.$$

Forms observed : $a = \{100\}$. $b = \{010\}$, $c = \{001\}$, $p = \{110\}$, $o = \{111\}$.
Cleavage : Perfect on $\{010\}$, less perfect on $\{100\}$.

FIG. 3.



Angles.

Angle.	n.	Measured.	Average.	Calculated.
110 : 010	22	44°38′—44°55′	44°47′*	—
110 : 111	14	28 5 —28 22	28 10 *	—
111 : 001	14	60 15 —60 40	60 34 *	—
010 : 001	11	89 49 —90 15	90 0	90° 0′
111 : $0\bar{1}0$	11	51 16 —52 8	51 47	51 48
100 : 111	—	—	—	51 4
110 : $1\bar{1}1$	8	89 38 —89 52	89 46	89 47

The habit of the crystals varies greatly with the conditions under which they have been formed. Those used for measurement, which were approximately of the habit shown in the figure, were obtained from solution in warm dilute alcohol. They were small and showed considerable irregularity in the development of the faces of one and the same form, giving a triclinic appearance. Larger crystals, formed by allowing the solution to stand over alcohol in a desiccator, were very irregular, and often had their edges and faces channelled out.

Crystals grown at the ordinary temperature from solutions containing much normal salt generally form thin, micaceous-looking plates, more or less tufted together, composed of the basal pinacoid bounded by narrow faces of $\{110\}$ and $\{010\}$. If large, these plates are not perfectly flat, but curved and irregular; they are not flexible, but break easily along the cleavages. These crystals are sometimes twinned on $\{110\}$. Crystals grown from slightly warm solutions with little normal salt sometimes form fairly thick, lozenge-shaped tables, the predominating basal pinacoid being bounded in this case principally by $\{111\}$, with $\{010\}$ also present. The form $\{100\}$ was of rare occurrence, and very narrow when present. The optic axes lie in a plane normal to the plane of symmetry; the acute bisectrix is nearly normal to {001}; and the axes are visible through this pinacoid, making a large angle, 2E = 113°.

Double refraction strong.

Potassium Trihydrogen Disuccinate, $KH_3(C_4H_4O_4)_2$.

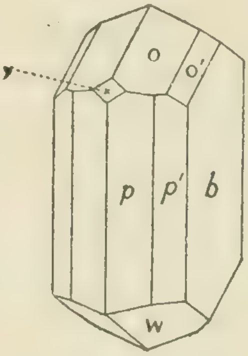
Crystal class: Monoclinic prismatic.

$$\beta = 94°36'.$$

$$a : b : c = 0{\cdot}9363 : 1 : 0{\cdot}4068.$$

Forms observed: $b = \{010\}$, $p = \{110\}$, $p' = \{210\}$, $y = \{301\}$, $o = \{111\}$, $o' = \{131\}$, $w = \{11\bar{1}\}$.

FIG. 4.



Cleavage: {010}, highly perfect, yielding thin, lustrous laminæ; these show additional cleavages parallel to the first and third axes, the latter being fibrous and evidently prismatic, the former probably pinacoidal, but owing to the nature of the substance this could not be made out with certainty; the crystals are very soft, and the cleaved laminæ are flexible.

Angles.

Angle.	*n*.	Measured.	Average.	Calculated.
$\bar{2}10 : \bar{1}11$	20	64° 3′—64°21′	64°14′ *	—
$111 : \bar{1}\bar{1}1$	12	41 49 —42 9	41 57 *	—
$111 : \bar{2}10$	15	82 16 —82 40	82 25 *	—
210 : 010	20	64 39 —65 18	64 56	64°59′
110 : 010	14	46 50 —47 42	47 7	46 59
131 : 111	1	—	27 36	27 27
010 : 111	7	70 5 —70 9	70 7	70 8
110 : 111	2	56 36 —56 40	56 38	56 48
$110 : \bar{1}11$	6	61 46 —61 52	61 49	61 47
210 : 111	2	57 29 —57 31	57 30	57 40
210 : 301	2	42 25 —42 35	42 30	42 40
301 : 111	2	32 53 —33 1	32 57	33 1
111 : 111	2	43 53 —43 57	43 55	43 47

The crystals are generally prismatic along the vertical axis, or tabular on the symmetry plane. Sometimes the two vertical prisms are about equally developed, but either may predominate greatly, even so as to practically extinguish the other. Sometimes the crystals are terminated by $\{11\bar{1}\}$ alone, sometimes $\{111\}$ is equally well developed or may predominate greatly; $\{301\}$ and $\{131\}$ occur comparatively seldom, though on some crystals the second of these was very prominent. On one crystal a single face of the first pinacoid $\{100\}$ was observed.

The form $\{010\}$ generally gives very good reflections, but the prism faces in the vertical zone are generally very much striated, and give multiple reflections so widely apart that they are practically useless for calculation. The best results for them were obtained on crystals grown in presence of succinic acid, the only condition under which the composition of the mother liquor remains constant. The only well-developed forms observed on these crystals were $\{210\}$, $\{010\}$ and $\{11\bar{1}\}$, and the angles obtained from them served as the basis for the calculations.

The plane of the optic axes is perpendicular to the plane of symmetry, b being the acute bisectrix; the obtuse bisectrix lies in the acute angle β', and, from the extinctions on cleavage plates, makes an angle of about 44° with the vertical $\cdot 2E = 122°50'$ at about 20°; it appears to increase appreciably with rise of temperature.

Double refraction negative, strong.

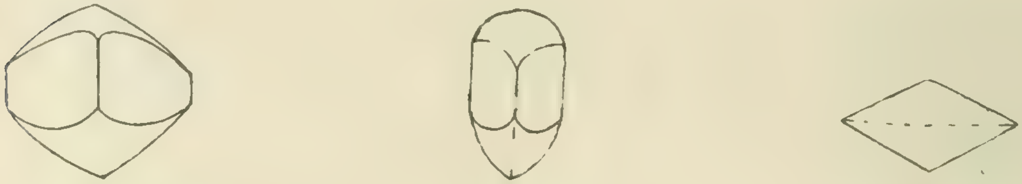
Crystals with Curved Boundaries.

Although it is not proposed to enter into this subject in detail now, a short statement of the principal phenomena may be of interest. These were first observed in an unsuccessful attempt to prepare potassium chromisuccinates corresponding to the chromioxalates. This observation led to the investigation of the effects produced by the presence of other substances in the solution, and it was found that many substances had a very pronounced effect in modifying the habit and appearance of the crystals of the potassium hydrogen succinates.

For the present, the effect of ferric compounds alone will be considered, as these give very definite results. If much ferric salt (chloride) is added to a solution of potassium hydrogen succinate, most of the iron is precipitated, but some remains dissolved or in colloidal solution. If the yellow solution is allowed to evaporate, the crystals of acid potassium salt which separate are coloured yellow and grow with curved surfaces instead of plane faces. If a crystal of the appropriate salt, grown from pure aqueous solution and bounded by plane faces, is removed and placed in the solution containing ferric salt, it continues to grow; but apparently its rate of growth along one particular direction is greatly impeded, with results which, shortly stated, are as follows:—

Hydrated Potassium Hydrogen Succinate.—The crystal growth becomes greatly restricted along the direction of the axis of symmetry, but takes place freely along the directions at right angles to it. The result is that the pinacoids entirely disappear, and the crystal is bounded laterally by the prism form only; the plane faces at the extremities become replaced by curved faces somewhat dome-shaped or conical in form, and distinctly different at the two ends, so that the crystal, when viewed along the three axes, presents the appearances shown below.

FIG. 5.



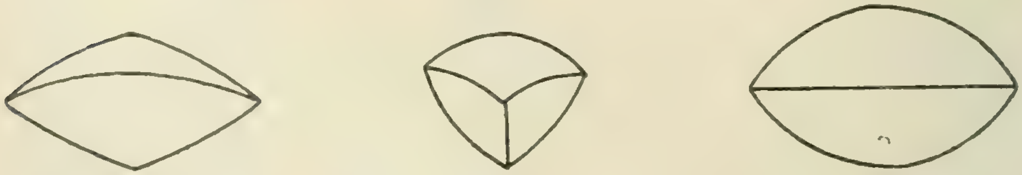
a. Front view. (Along *a.*)

b. Side view. (Along *b.*)

c. Bottom view. (Along *c.*)

If the crystal is allowed to continue its growth in this solution, the prism faces gradually disappear and the resulting form is entirely devoid of plane faces; the upper bounding surface has an elliptical dome-shaped appearance, whilst the lower one is more conical, but is distinctly ridged along the trace of the central plane parallel to $\{100\}$; the appearance now is approximately that shown below.

FIG. 6.



a. Front view.

b Side view.

c. Bottom view.

It is to be observed that throughout these changes the shapes maintain the symmetry characteristic of the rhombic pyramidal class, notwithstanding the absence of plane faces.

Potassium Trihydrogen Disuccinate.—A crystal of this salt placed in an appropriate solution containing ferric compound undergoes a metamorphosis more or less analogous to that just described, the ultimate result being the production of what might be called a monoclinic "bi-cone," consisting of two cones, approximately elliptical in section, applied base to base, with the line joining the two apices inclined obliquely to the common base. The figure here also displays the symmetry characteristic of the original crystal. The major axis of the oval base lies in the plane of symmetry, and generally appears to be considerably longer than the other, so that the two are not proportional to the axial ratios already given for the salt; further, the axis joining the apices makes with the base an angle decidedly greater than β. If the crystal is left in the solution after the plane faces have disappeared, it continues to grow out laterally, so that the cones become much more obtuse.

In both cases the crystals grown from ferric solution contain a small percentage of iron, generally decidedly more in the second case, as the more acid solution can retain more ferric compound than the less acid one. In no case were the crystals found to contain more than 0·5 per cent. of Fe_2O_3. In what form the iron is present in the solid solution it is difficult to decide; so also is the question whether the peculiar growth of the crystals is due to the presence of this ferric compound in the crystals, to its presence in the solution, or to both. It is hoped that the subsequent work will help to elucidate these points, and throw some light on the general question of the formation of curved boundaries on crystals.

The work here described was begun in the Chemistry Department of the University of Edinburgh, and has been continued partly there and partly at Surgeons' Hall, Edinburgh, and University College, London, and we desire to express our thanks to Mr. James Kerr, B.Sc., and Sir William Ramsay, K.C.B., F.R.S., for the facilities they have granted. We are also indebted to the Carnegie Trust for grants towards carrying on the investigation.

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CXLVI.—*The Relation between Absorption Spectra and Optical Rotatory Power. Part II. The Tartaric Acids.*

By ALFRED WALTER STEWART, D.Sc. (Carnegie Research Fellow).

IN a previous paper (Trans., 1907, **91**, 199), the author has dealt with the relation between the general absorptive powers of various substances and their influence on the optical rotatory power of an active radicle; and has shown that of two isomeric substances the one which possesses the greatest absorption has also the greatest effect on rotation. The present paper deals with the absorption spectra of the four forms of tartaric acid. Some of these have already been dealt with by Magini (*J. Chim. phys.*, 1904, **2**, 410), but that author appears to have missed a most interesting point.

When we consider the configurations of these four substances, we find that three of them present no difficulty. From previous work on the subject, it seems evident that the absorption spectrum of a substance is influenced chiefly by four factors: the elements of which it is composed, the manner in which the atoms are linked together, the arrangement of the atoms in space, and the amount of substance through which the light passes before it reaches the spectroscope. Since in the tartaric acids the first, second, and fourth factors are constant when the complete absorption spectrum is plotted, we have only to consider the third factor.

Now in the dextro- and lævo-forms of tartaric acid we have two configurations which, although related to one another as object and mirror-image, are identical if we take into account only the distances between the mean positions of the various atoms. The mean distance between the carboxyl groups in *d*-tartaric acid is probably the same as that between the carboxyl groups in *l*-tartaric acid, otherwise their conductivities would not be identical; and since the physical measurements of the spectroscope are not affected by molecular enantiomorphism any more than a conductivity measurement is, we should expect to find the spectra of *d*- and *l*-tartaric acids identical.

The case is quite otherwise when we turn to the internally compensated form, mesotartaric acid. Here the two halves of the molecule, instead of being identical (as in the case of the active radicles), are mirror-images of each other. The distances between the various radicles in mesotartaric acid are therefore different from the corresponding distances in the active forms, and the spectra of the active and meso-forms might be expected to differ from each other just as their conductivities do. This probability is strengthened by the known differences between the spectra of structurally identical, but stereoisomeric unsaturated acids, which were dealt with in the preceding paper.

When we examine the case of the racemic form, however, we are left without any such guide. The formation of racemic acid from the two active isomerides cannot be supposed to take place by any ordinary addition reaction such as the formation of a salt, for if an oxonium salt were formed from two molecules of racemic acid, there seems no reason why a similar salt should not be formed from two molecules of one antipode. In the light of evidence, which will be dealt with later in this paper, it seems probable that the process is analogous to double salt formation, although it is governed by spacial factors which do not enter into ordinary double salt formation. Except by a coincidence, it is hardly to be expected that the spectrum of a true racemic compound would be identical with that of the corresponding active or meso-form; but we must take another possibility into account, namely, the chance that in a given solution the racemic compound may dissociate into its two components, and thus show an absorption spectrum which need not differ from that of either active form.

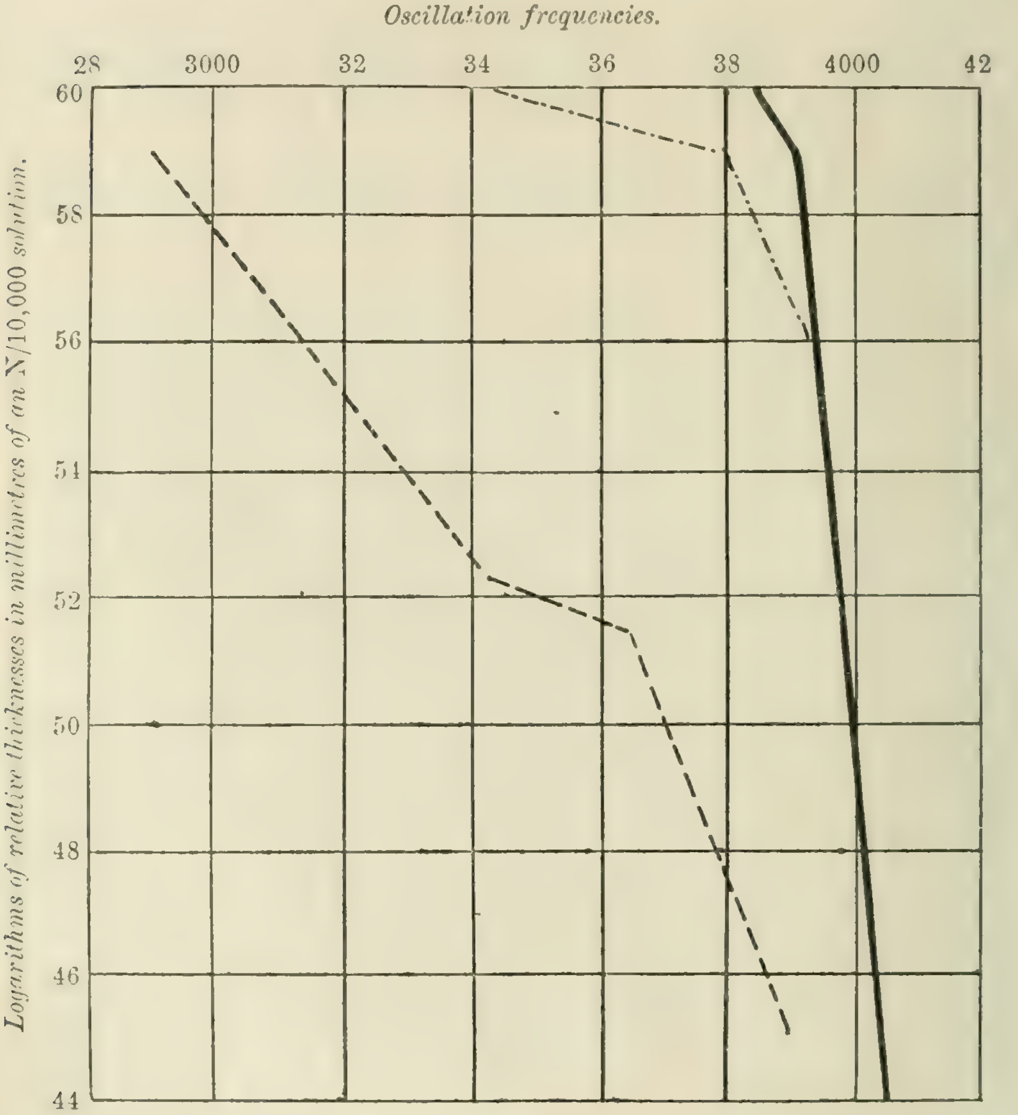
It was with the view of obtaining information on this last point that the following investigation was undertaken, the results of which may now be given.

In the first place we may deal with the spectrum of *d*-tartaric acid in aqueous solution, which is indicated in the figure by the full curve. No absorption band is shown in the spectrum within the range of concentration used in the experiments. The identity of the spectra of the dextro- and lævo-acids will be shown later.

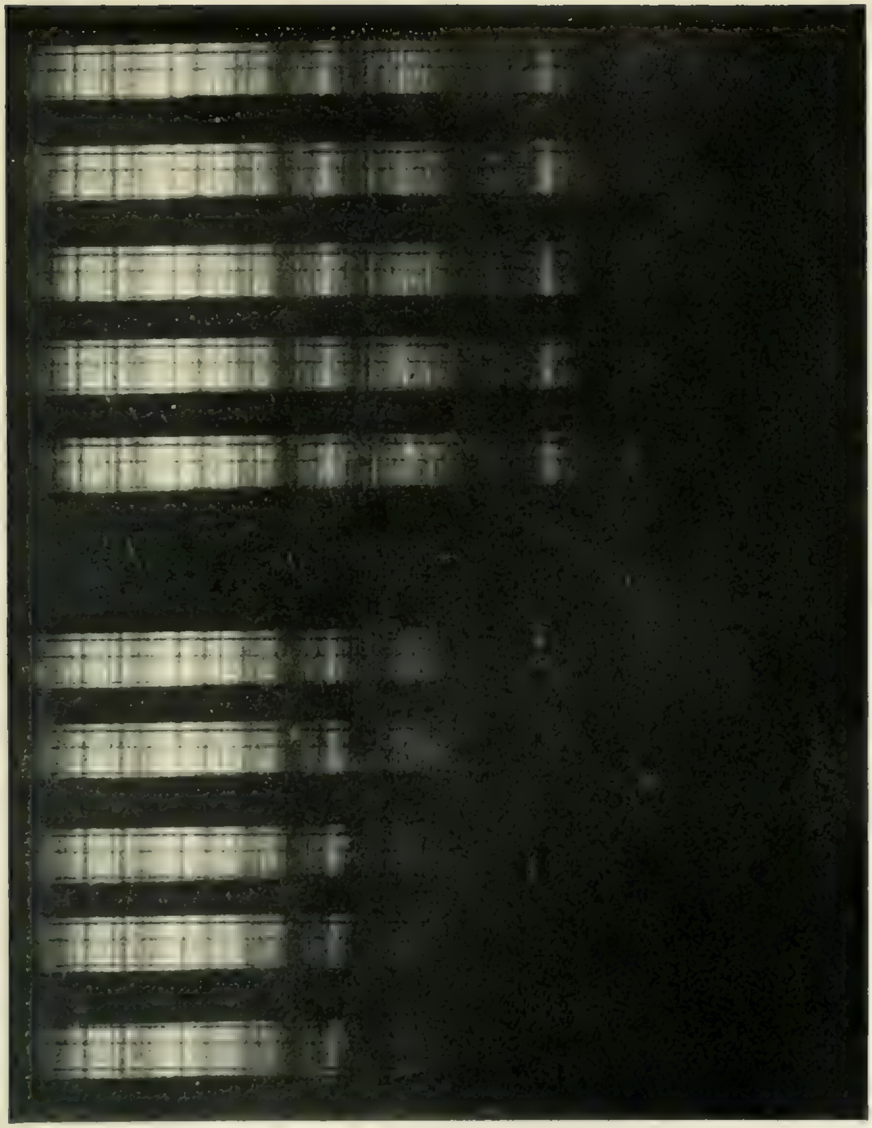
When equal volumes of equally concentrated solution of *d*- and *l*-tartaric acids are mixed, there are two possibilities to be taken into account. In the first place, the antipodes may not combine with one another, but may remain separate in the solution. In this case the spectrum of the solution might be expected to be the same as that of a solution of one antipode of the same concentration. On the other hand, if the two antipodes combine to form a racemic compound, the resulting solution will have only half the molecular concentration of the original antipodic solutions; for a mixture of 1 litre of normal *d*-tartaric acid solution with 1 litre of normal *l*-tartaric acid solution will give rise to 2 litres of a racemic acid solution which contains only 1 gram-molecule of racemic acid, that is, a semi-normal solution. In this case, if the absorption spectrum of racemic acid were at all like that of the active acids, we should expect to find the absorption produced by a mixture of the dextro- and lævo-solutions, to be weaker than that shown by an equal thickness of an active solution.

An examination of the figure and plate will show that neither forecast was correct. When a solution of racemic acid was substituted for that of the active form and the iron arc spectrum rephotographed through the same thicknesses as had previously been employed, it was found that the inactive solution had a greater absorption than the active isomeride. In the figure, this is shown by the dot-and-dash curve. The difference between the spectra can be seen in the plate, which represents the results of five exposures of each compound. The upper set, showing but little absorption, were obtained by photographing through a normal solution of *d*-tartaric acid, the thicknesses chosen being 100, 95, 90, 85, and 80 millimetres, whilst the lower set shows the effect of substituting racemic acid for the active form.

Somewhat similar results were found in the case of *d*- and *l*-limonene and dipentene, but as the purity of these substances is at present in dispute, it is unnecessary to give the curves here. The dextro- and lævo-compounds had not quite identical spectra, probably owing to the presence of some impurity; but an equimolecular mixture of the two showed a greater absorptive power than either alone.



Broken line curve = *Mesotartaric acid.*
Full ,, = *Dextro- and lævo-tartaric acid.*
Dot and dash ,, = *Racemic acid after divergence from curve of active forms.*



To face p. 1540.

The upper spectra are those of dextro-tartaric acid.
The lower ,, ,, racemic-tartaric acid.

In each case the iron arc was photographed through 100, 95, 90, 85, and 80 millimetres of a normal solution of the acid.

An examination of the racemic acid spectrum brings to light some points of interest. In the first place, just above the abscissa 58, there is a considerable increase in absorption, which is shown in the curve by its deviation to the left. No such absorption is to be found in the spectra of the active isomerides. The second point of interest is to be found in the fact that at low concentrations the spectra of racemic acid and active tartaric acids are identical. This is in agreement with the evidence derived from the work of Raoult (*Zeitsch. physikal. Chem.*, 1887, **1**, 186), Ostwald (*J. pr. Chem.*, 1885, [ii], **32**, 341), and Marchlewski (*Ber.*, 1892, **25**, 1556); for it is well known that if a 14 per cent. aqueous solution of racemic acid is prepared, 13·9 per cent. of the acid breaks up into active tartaric acids, and this decomposition is even more complete in dilute solutions. From this it is apparent that the curve given in the figure cannot represent the true absorption spectrum of racemic acid, although it is probably as near it as can be found. It should be pointed out that the curve shown in the figure is calculated on the basis that the molecular weight of racemic acid, including its water of crystallisation, is 168. If the double molecule (molecular weight, 336) be taken as a basis, then the absorption would naturally be much greater still. It is evident, further, that the spectra of the dextro- and lævo-forms must be identical, as a solution of a mixture of them possesses the same absorptive power as that of one isomeride of the same concentration. If they were not identical, the curve of the diluted racemic acid solution could not coincide exactly with that of the active tartaric solution.

The above observations are confirmed by the work of Byk (*Zeitsch. physikal. Chem.*, 1904, **59**, 682), in which he found that alkaline solutions of copper tartrate and copper racemate differed slightly in colour.

Turning now to the spectrum of mesotartaric acid, which is shown in the figure by the broken curve, it is evident that this substance exerts an even greater absorptive power than the racemic compound. Like the others, this spectrum also appears to contain no absorption band. In accordance with the theoretical views laid down in the beginning of this paper, the meso-form has a spectrum quite different from that of the active forms.

From a consideration of the foregoing experimental results, certain points of interest suggest themselves. In the first place, it seems desirable to find out whether or not the increase of absorptive power found in the case of a mixture of antipodes was noticeable in the case of other stereoisomerides. With this end in view, the spectrum of an equimolecular mixture of maleic and fumaric acids was photographed and compared with the spectra of the pure substances. In this case the absorption curve lay between those of maleic and fumaric acids, which probably indicates that a mere mixture of the substances is present in this case.

There is, however, another way in which the subject may be regarded. A double salt above and below its temperature of transition furnishes the closest parallel to a solution which may contain either a mixture of two antipodes or a racemic compound. The spectrum of astrakanite was therefore examined above and below 22°, and it was found that below this temperature, when the double salt was present, the absorption shown is different from that found above 22°. It is unnecessary to give the curve at present as it will be published later in a paper dealing with the application of this method to the detection of transition temperatures.

Many applications of this work to stereochemical problems at once suggest themselves. In the first place, it may be pointed out that even at the present time it is extremely difficult to ascertain whether a substance is a true racemic compound or a mere mixture of the two antipodes. As has already been mentioned in this paper, a determination of the molecular weight furnishes no great assistance, since at low concentrations the racemic form may break down into the two active forms; there appears to be no information to be gained from vapour density determinations (Anschütz, *Ber.*, 1885, **18**, 1398), from the rise in temperature when the two antipodes are mixed (Berthelot and Jungfleisch, *Ann. chim phys.*, 1875, [v], **4**, 147; Pickering, Trans., 1887, **51**, 367), or from the change in volume under the same circumstances (Marchlewski, *Ber.*, 1892, **25**, 1561); and in the case of liquid racemic compounds the criteria of the melting point cannot be utilised. As has been shown in the present paper, the spectroscope furnishes a means of distinguishing between a true racemic compound and a mixture of the two antipodes.

In the second place, it is occasionally necessary to determine the existence limits of a given racemic compound, and the methods at present at our disposal are somewhat tedious. It seems simpler, when a transition point is suspected within a given range of temperature, to take two photographs, one at each end of the temperature range, and compare the spectra thus obtained. If they are identical, no transition point exists within these limits.

A third possible application is to be found in the case of pseudoracemic compounds, the existence of which is in some cases disputed.

The following facts have been established in the course of this work:

I. The spectra of the two active forms of tartaric acid are identical.

II. The spectrum of mesotartaric acid shows greater general absorption than that of the active isomerides. This confirms the dependence of the absorption spectrum on the space arrangement of atoms, to which attention was drawn in the previous paper.

III. True racemic acid is present in highly concentrated solutions, but breaks down as they are diluted. The racemic form has a greater general absorption than the active forms.

IV. From the spectroscopic point of view, racemic acid and the active tartaric acids stand in the same relation to each other as a double salt to its components.

V. No similar double compound is formed when solutions of maleic and fumaric acid are mixed.

The author desires to thank Mr. E. C. C. Baly for the loan of his spectroscope.

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CXLVII.—*The Wandering of Bromine in the Chlorination of Bromoanilines.*

By WALTER WILLIAM REED and KENNEDY JOSEPH PREVITÉ ORTON.

IN the course of an investigation on the changes undergone by the diazonium salts of *s*-chlorobromodiazobenzenes (this vol., p. 1554) it became necessary to prepare 2 : 6-dichloro-4-bromoaniline. But the compound which was obtained by chlorinating *p*-bromoaniline yielded a diazo-derivative behaving in an anomalous manner; we were thus led to examine the aniline, produced in this way from *p*-bromoaniline, more closely.

This base was originally isolated by Fittig and Büchner (*Annalen*, 1877, **188**, 22) from the products of the action of chlorine on *p*-bromoaniline in hot concentrated hydrochloric acid solution. Purification by recrystallisation from alcohol gave a well crystallised product melting at 93·5°.

In the first instance, we repeated Fittig and Büchner's preparation, and after several crystallisations obtained a material having the melting point recorded by them. On analysis, however, this substance, which had in all respects the characters of a *s*-trisubstituted aniline, was found to have too low a percentage of chlorine and too high a percentage of bromine. Inasmuch as tetrachloro-*p*-quinone is formed in this chlorination, it is obvious that bromine is eliminated, which may then brominate some of the *p*-bromoaniline. In order to avoid this displacement of bromine and the oxidation of the aniline to quinone, we modified Fittig and Büchner's procedure, in that we used a cold solution of the *p*-bromoaniline in 20 per cent. hydrochloric acid and, instead of passing chlorine gas into the solution, added the calculated quantity of chlorine dissolved in the same medium. Under these conditions, all the *p*-bromoaniline was entirely converted into trihalogen-aniline, very little, if any, oxidation occurring. The product had an indefinite melting point, 70—81°, but on analysis gave numbers corresponding to a dichlorobromoaniline. On repeated recrystallisation from alcohol, a substance was isolated melting at 93°, and apparently identical with Fittig and Büchner's compound. Analysis of this material, however, showed too high a percentage of bromine, 41·4 per cent., whilst a dichlorobromoaniline requires 33·19 per cent.

Since the *p*-bromoaniline is treated with the calculated quantity of chlorine and no chlorine or mono- or di-substituted aniline remains, it follows that, besides the normal product of chlorination, the dichlorobromoaniline, *s*-trichloroaniline must have been produced in amount equivalent to the chlorodibromoaniline.* The reactions would then be represented by the two equations:

$$C_6H_4Br{\cdot}NH_2 + 2Cl_2 = C_6H_2Cl_2Br{\cdot}NH_2 + 2HCl.$$
$$2C_6H_4Br{\cdot}NH_2 + 4Cl_2 = C_6H_2Cl_3{\cdot}NH_2 + C_6H_2ClBr_2{\cdot}NH_2 + 4HCl.$$

All attempts to separate the mixture of the anilines by treatment with solvents failed. Analysis of the less soluble fractions, which had the highest melting points, showed that chlorodibromoaniline was present, whilst that of the most soluble fractions, with the lowest melting points, indicated the presence of *s*-trichloroaniline. Intermediate crystalline fractions could be obtained (melting at 82—84°), analysis of which gave numbers corresponding to a dichlorobromoaniline, but these materials could always be resolved on further recrystallisation into lower and higher melting fractions with the characters just described.

Attempts were made to throw light on the composition of the mixture and to effect a separation of the anilines, on the one hand, by converting the bases into the acetyl derivatives (which could be fractionated from alcohol) and these into the chloroamino-derivatives, Ar·NClAc, which were then fractionated from light petroleum, and, on the other hand, by converting the anilines into the nitroaminobenzenes, $Ar{\cdot}NH{\cdot}NO_2$, the barium salts of which were fractionally crystallised from water. These lines of attack confirmed the above conclusions; the less soluble fractions contained a chlorodibromo-compound in proportions varying with the treatment from 35 to 50 per cent.

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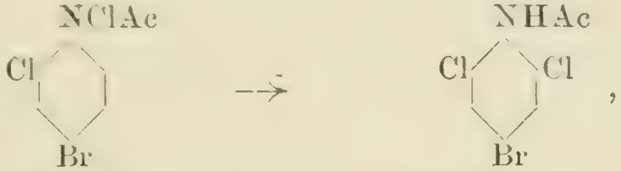
* It is possible that a small quantity of *s*-tribromoaniline is formed in this chlorination, but no evidence of its presence was obtained.

Chlorination in anhydrous solvents, benzene, chloroform, or carbon tetrachloride, either with the calculated quantity or with excess of chlorine, led to the same result. In one particular, the use of these media caused a difference; all the base present was not converted into a *s*-trisubstituted aniline, some remaining unchanged or becoming only mono-chlorinated.

2 : 6-Dichloro-4-bromoaniline was finally prepared in a pure state by two different methods. Acetylchloroamino-2-chloro-4-bromobenzene changes nearly quantitatively into 2 : 6-dichloro-4-bromoacetanilide when heated to 130° under pressure:



no displacement of bromine apparently occurring.

The second method is based on the fact that acetylchloroaminobenzenes react with anilines, yielding acetanilides and chloroanilines. In this way, *p*-bromoaniline can be readily chlorinated by acetylchloroamino-2 : 4-dichlorobenzene, which is the most convenient chloroamine for the purpose:

$$C_6H_4Br{\cdot}NH_2 + 2C_6H_3Cl_2{\cdot}NClAc = C_6H_2Cl_2Br{\cdot}NH_2 + 2C_6H_3Cl_2{\cdot}NHAc.$$

Although in the latter reaction bromine may, to a small extent, be displaced, it is possible, when due regard is paid to conditions of concentration and temperature, to avoid this completely.

The action of chlorine on other bromoanilines has also been investigated, *o*- and *m*-bromoaniline and 2 : 4- and 2 : 6-dibromoaniline being used. As was to be expected, *m*-bromoaniline yields quantitatively 2 : 4 : 6-*trichloro-3-bromoaniline*, which has not been hitherto described; similarly, *o*-bromoaniline and 2 : 6-dibromoaniline give respectively 4 : 6-dichloro-2-bromo- and 4-chloro-2 : 6-dibromo-aniline. 2 : 4-Dibromoaniline, however, behaves as does *p*-bromoaniline; a mixture of anilines is obtained, from which high melting, less soluble, fractions containing *s*-tribromoaniline and low melting, more soluble, fractions containing a dichlorobromoaniline can be isolated.

It is obvious that the susceptible position is the para, relative to the amino-group. Under the conditions, namely, treatment of the aniline dissolved in 20 per cent. hydrochloric acid with the calculated quantity of chlorine dissolved in the same medium, simple chlorination of an aniline having an ortho-position unoccupied but bromine in the para-position, does not occur. Some displacement of this para-bromine atom is always found, but so far as experiments have been made, a similar displacement of an ortho-bromine atom is not observed in the absence of excess of chlorine. Moreover, it should be noted that this displacement of bromine is not a step in a more or less profound oxidation of the aniline by the aqueous chlorine; no oxidation takes place under the conditions here fixed, but a simple replacement by the chlorine of the bromine, which then rebrominates another molecule (or possibly the same) of aniline.

The mutual replacement of chlorine and bromine in anilines was first observed by Wegscheider (*Monatsh.*, 1897, **18**, 329), who converted *s*-tribromoaniline into *s*-trichloroaniline by treatment with hydrochloric acid at 240°. He obtained evidence of a similar replacement of chlorine by bromine on heating *s*-trichloroaniline with hydrobromic acid. Chattaway and Orton (Trans., 1901, **79**, 822) investigated the action of acetylchloroaminobenzenes on *s*-trihalogenanilines and found that chlorine replaced one atom of bromine, that in the para-position relative to the amino-group apparently being mainly concerned.

It will not be out of place to give a list of the melting points (corr.) of the *s*-chlorobromoanilines and their acetyl derivatives, which have all been prepared and purified by us with special care in the light of the knowledge acquired in this research.

	M. p.
2 : 4-Dichloro-6-bromoaniline	81·5—82°
2 : 4-Dichloro-6-bromoacetanilide	216
2 : 6-Dichloro-4-bromoaniline	85
2 : 6-Dichloro-4-bromoacetanilide	204—205
6-Chloro-2 : 4-dibromoaniline	99
6-Chloro-2 : 4-dibromoacetanilide	227
4-Chloro-2 : 6-dibromoaniline	95·5
4-Chloro-2 : 6-dibromoacetanilide	226

With the exception of 2 : 6-dichloro-4-bromoaniline, these melting points are substantially in agreement with those previously recorded. It is of interest to note the melting points of mixtures of isomeric anilines or anilides. The melting-point curves of such mixtures are nearly, but not quite, straight lines. Thus a mixture of 2 : 4-dichloro-6-bromo- and 2 : 6-dichloro-4-bromo-aniline containing 50 per cent. of each aniline melts at 79·5°. In the case of similar mixtures of a chlorodibromo- and a dichlorobromo-aniline, the melting-point curves have a similar form.

EXPERIMENTAL.

Chlorination of p-*Bromoaniline and of 2-Chloro-4-bromoaniline.* (2 : 6-*Dichloro-4-bromoaniline.*)

Fittig and Büchner (*loc. cit.*) chlorinated *p*-bromoaniline, dissolved in hot concentrated hydrochloric acid. They isolated from the product a chlorobromoaniline (2-chloro-4-bromoaniline ?) and a small quantity of a substance resembling tetrachloro-*p*-quinone, and, finally, a substance which they took to be a *s*-trisubstituted aniline, 2 : 6-dichloro-4-bromoaniline. They found that when heated it changed at 80° and melted at 93·5°.

In our attempts to prepare 2 : 6-dichloro-4-bromoaniline for the purposes mentioned in the foregoing, we repeated Fittig's experiments, but found that the aniline was contaminated with so much highly coloured oxidation products (quinones and azo-compounds) that the yield was small and the purification difficult. We tried therefore the following modifications of the method.

Experiment 1.—The aniline, dissolved in 10 per cent. hydrochloric acid, was treated with chlorine water, using the calculated quantity of chlorine. On the addition of the chlorine, a red, oily material immediately separated, which did not offer any prospect of an easy isolation of the chlorinated aniline.

Experiment 2.—The aniline was dissolved in concentrated (35 per cent.) hydrochloric acid and chlorine water added. It this case it was noted at first that the colour of chlorine persisted, chlorination not appearing to take place until the hydrochloric acid had been diluted. The product was still highly coloured, and was purified by distillation in steam. It then melted at 86°, and, after recrystallisation from alcohol, at 89—90°.

Experiment 3.—The chlorination was carried out as in the last experiment, but the chlorine solution was made up in concentrated (35 per cent.) hydrochloric acid, when it was found that no chlorination whatever occurred until water was added, that is, until the hydrochloric acid was diluted. The product in this case was identical with that obtained in Experiment 2.

Experiment 4.—Twenty-four per cent. hydrochloric acid * was substituted as solvent for the 35 per cent. acid ; chlorination now occurred, but a certain amount of oxidation also took place. The product had the same characters as in the previous experiments.

Experiment 5.—Owing to the insolubility of the hydrochloride of

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* A saturated solution of chlorine in 24 per cent. hydrochloric acid at 15° is a 0·33*N*-solution. It is unstable and must be freshly prepared when used as a chlorinating agent.

p-bromoaniline in 24 per cent. hydrochloric acid, 20 per cent. hydrochloric acid was used. Chlorination took place rapidly, the amount of oxidation not being materially increased by using the more dilute acid. The procedure was as follows: 0·1 gram-molecule (17·2 grams) of *p*-bromoaniline was dissolved in 1 litre of 20 per cent. hydrochloric acid. To this solution, which was vigorously stirred with the aid of a turbine, 1396 c.c. of a 0·32*N*-solution of chlorine in 20 per cent. hydrochloric acid (that is, 5 per cent. excess of the calculated quantity, 0·2 gram-molecule) was slowly run in. As the chlorine was introduced, a slight red coloration developed; after the mixture had been kept for a few minutes, a few c.c. of sulphurous acid were added in order to remove the excess of chlorine. The solution was then diluted with 1280 c.c. of water, whereupon the chlorinated product separated in small, slightly coloured needles, weighing 8·7 grams, and melting at 78—83°.

The diluted mother liquor was distilled, and the solid which passed over was collected in two fractions; fraction 1 (2·74 grams), which was by far the larger, melted at 68—72°, and fraction 2 (0·4 gram) at 78—83°.

The original crystalline separation (m. p. 78—83°) and fraction 2 (m. p. 78—83°) were treated together and crystallised repeatedly from 95 per cent. alcohol. The melting point rose quickly, and, after two recrystallisations, 1 gram, melting at 91—92°, was obtained, which remained unchanged on further recrystallisation. This material, which crystallised in long colourless needles, was analysed:

0·1633 gave 0·3058 AgCl + AgBr and 0·2618 AgCl. Cl = 18·17; Br = 48·40.

$C_6H_4NClBr_2$ requires Cl = 12·43; Br = 56·04.

$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·19 per cent.

These numbers indicate that the material is a mixture of a dichlorobromoaniline and a chlorodibromoaniline of the composition:

$C_6H_2Cl_2Br{\cdot}NH_2$ = 35·28, and $C_6H_2ClBr_2{\cdot}NH_2$ = 64·72 per cent.

Fraction 1 (m. p. 68—72°) yielded on recrystallisation from 75 per cent. alcohol a small amount of a material melting at 82°, analysis of which gave numbers in agreement with those required by a dichlorobromoaniline, but this material on further crystallisation from 95 per cent. alcohol was resolved into fractions, the less soluble of which melted above 90°.

As was shown in the foregoing, since a chlorodibromoaniline is formed and sufficient chlorine was used to chlorinate the *p*-bromoaniline completely, it is obvious that *s*-trichloroaniline must be among the products of the reaction. Of the mother liquors from the various fractions. the first and second from the material melting at 68—72° alone yielded a substance melting below 80°. From these, a well crystallised substance melting at 72—77° was obtained in small quantities, and shown to contain no mono- or di-substituted aniline by extraction with 10 per cent. hydrochloric acid. These crystals gave the following numbers on analysis:

0·1164 gave 0·2368 AgCl + AgBr and 0·228 AgCl. Cl = 37·74; Br = 21·60.

Assuming that the material is a mixture of dichlorobromoaniline and *s*-trichloroaniline, this result gives the composition:

$$C_6H_2Cl_2Br\cdot NH_2 = 65{\cdot}46, \text{ and } C_6H_2Cl_3\cdot NH_2 = 34{\cdot}54 \text{ per cent.}$$

Chlorination in Anhydrous Solvents.

Both *p*-bromoaniline and 2-chloro-4-bromoaniline were treated with chlorine in benzene and carbon tetrachloride solution; in some experiments chlorine gas was passed into the solution, that is, excess of chlorine was used, in others, a solution of the calculated quantity of chlorine in the solvent was employed. Inasmuch as insoluble hydrochlorides are formed, it is difficult to ensure complete chlorination. This difficulty is the greater the drier the solvent and the chlorine. Apparently the insoluble hydrochlorides are attacked more easily in the presence of small quantities of water.

The product of the reaction, obtained in all experiments, when freed from material incompletely chlorinated, melted at 76—80°, and on repeated crystallisation from 95 per cent. alcohol yielded small amounts of a well crystallised substance melting at 93°. Analysis indicated that this was the same mixture as was obtained in the chlorination in hydrochloric acid.

Attempts at Indirect Separation of the Mixture of Anilines.

1. An attempt was made to isolate the chlorodibromoaniline from the mixture by converting the anilines into the nitroamines and fractional crystallisation of the barium salts from water.

A considerable quantity of the mixture was nitrated with a mixture of nitric acid and acetic anhydride in acetic acid solution (Orton, Trans., 1902, **81**, 806). The barium salt was recrystallised from boiling water until the quantity had been reduced to 0·8 gram, when it was reconverted into the nitroamine. Analysis of the latter showed that, although the nitroaminochlorodibromobenzene had become concentrated in the less soluble fractions, nitroaminodichlorobromobenzene was still present.

2. Acetylation of the mixture of anilines and fractional recrystallisation of the anilines gave the same results as recrystallisation of the anilines. The least soluble fraction melted at 212—214° and, on analysis, showed the presence of much chlorodibromoacetanilide; the

more soluble fractions melted at 199—201° and contained a higher percentage of chlorine than is required by a dichlorobromoacetanilide.

The fractions of lower melting point, of which a considerable quantity was collected, were converted into the chloroamine, which was then fractionated from petroleum. The separation which was thereby achieved differed in no way from that which resulted in the fractionation of the anilines or anilides.

Preparation of 2 : 6-*Dichloro-*4-*bromoaniline. Chlorination of* p-*Bromoaniline by Means of Acetylchloroamino-*2 : 4-*dichlorobenzene.*

The calculated quantity of the chloroamine (2 gram-molecules, 5·8 grams) dissolved in 15 c.c. of chloroform is added to a solution of the *p*-bromoaniline (1 gram-molecule, 2 grams) in 15 c.c. of chloroform. The mixture should be warmed to bring about the reaction, which may often become violent; for this reason it is inadvisible to use larger quantities. On completion of the reaction, the solution is cooled, whereupon much of the 2 : 4-dichloroacetanilide separates. After filtering, dry hydrogen chloride is passed into the mother liquor, the hydrochloride of dichlorobromoaniline together with that of the 2 : 4-dichloroacetanilide separating. After collection and washing with chloroform, the hydrochlorides are boiled with 75 per cent. alcohol containing 5 per cent. of concentrated hydrochloric acid. The anilide is thereby hydrolysed, and, on cooling, the dichlorobromoaniline separates in long, colourless needles, whilst the more basic dichloroaniline remains in the acid solution. The needles melted constantly at 85° and gave on analysis the following numbers:

0·2242 gave 0·4419 AgCl + AgBr. Cl + Br = 62·63.

0·1693 ,, 0·3326 AgCl + AgBr and 0·3017 AgCl. Cl = 29·52; Br = 32·78.

$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·19 per cent.

2 : 6-*Dichloro-*4-*bromoacetanilide.*—The aniline is readily acetylated by heating in acetic acid solution with some excess of acetyl chloride, when it is obtained in colourless, elongated prisms melting at 204—205°.

The anilide can also be prepared from acetylchloroamino-2-chloro-4-bromobenzene, which undergoes molecular rearrangement when heated under pressure at 130° for four hours. The product, which was highly coloured, was recrystallised first from benzene and then from alcohol, when it melted constantly at 204—205°:

0·3162 gave 0·5277 AgCl + AgBr and 0·36 Ag. Cl = 24·93; Br = 28·11.

$C_8H_6ONCl_2Br$ requires Cl = 25·06; Br = 28·26 per cent.

*Acetylchloroamino-*2 : 6-*dichloro-*4-*bromobenzene*, $C_6H_2Cl_2Br{\cdot}NClAc$.—The chloroamine was prepared from the pure anilide as follows.

1·2 Grams of the anilide were dissolved in 30 c.c. of warm glacial acetic acid and some excess of a 0·68*N*-solution of bleaching powder slowly added. On cautiously diluting and cooling the mixture, the chloroamine crystallised in lustrous plates; from petroleum it crystallises in short, rectangular prisms or porcelain-like aggregates of these melting at 81°:

0·2039 liberated iodine equivalent to 12·4 c.c. *N*/10 iodine. Cl as $\colon$NCl = 10·8.
$C_8H_5ONCl_3Br$ requires Cl as $\colon$NCl = 11·17 per cent.

1-*Nitroamino*-2 : 6-*dichloro*-4-*bromobenzene*, $C_6H_2Cl_2Br\cdot NH\cdot NO_2$.—To a solution of 0·75 gram of the pure dichlorobromoaniline in 20 c.c. glacial acetic acid, 1 c.c. of nitric acid (87 per cent.), rendered free from nitrous acid by addition of carbamide nitrate, was added. Acetic anhydride (2 c.c.) was then slowly introduced, whereupon the aniline nitrate dissolved. The solution was poured into water and the crude nitroamine which separated was collected, washed with water, and dissolved in aqueous sodium carbonate. This solution was warmed with charcoal, filtered, diluted with 700 c.c. of boiling water, and then acidified with hydrochloric acid. On cooling, the nitroamine separated in long, colourless needles melting and decomposing at 132°:

0·1817 gave 0·2999 AgCl + AgBr. Cl + Br = 52·45.
$C_6H_3O_2N_2Cl_2Br$ requires Cl + Br = 52·75 per cent.

The *barium* salt had the same characters as those of similar constituted nitroamines.

Chlorination of 2 : 4-*Dibromoaniline.*

2 : 4-Dibromoaniline was chlorinated in hydrochloric acid solution in the manner previously described, using the calculated quantity of chlorine, namely, 1 gram-molecule. No chlorine remained in the solution and no coloration was observed. On addition of water, the product was precipitated in small needles, which melted at 95—97°. Five grams of this material were dissolved in so much boiling alcohol that 1 gram separated on cooling. The latter, which was in the form of long, colourless needles, melted at 105—106°, and yielded on similar treatment 0·2 gram of crystals melting at 110°. Pure 2-chloro-4 : 6-dibromoaniline melts at 99°, whilst *s*-tribromoaniline melts at 120°. On the assumption that only chlorodibromoaniline and *s*-tribromoaniline are present, analysis showed that the mixture (m. p. 110°) contained 59·3 per cent. of the latter:

0·2096 gave 0·3659 AgCl + AgBr and 0·2897 AgCl. Cl = 5·1; Br = 65·3.
$C_6H_4NClBr_2$ requires Cl = 12·43; Br = 56·04 per cent.

The mother liquors yielded a final fraction melting at 92—94°; analysis showed it to contain the dichlorobromoaniline, which must be formed together with the tribromoaniline.

Chlorination of o-*Bromoaniline.*

The *o*-bromoaniline, dissolved in 20 per cent. hydrochloric acid, was treated with 2 gram-molecular proportions of chlorine dissolved in the same solvent, and the product precipitated with water. Small, white needles were obtained which melted at 81·5°, this melting point being only raised to 82° on recrystallisation from alcohol. Analysis gave numbers corresponding to the pure 2 : 4-dichloro-6-bromoaniline, which melts at 81·5—82°.

Chlorination of 2 : 6-*Dibromoaniline.*

2 : 6-Dibromoaniline was treated with a solution of chlorine in the same way, 1 gram-molecular proportion of chlorine being used. The crude product melted at 94°, and was not changed by crystallisation from alcohol. 4-Chloro-2 : 6-dibromoaniline melts at this temperature, and analysis showed that the substance had the composition of this aniline.

2 : 4 : 6-*Trichloro-3-bromoaniline.*

m-Bromoaniline is readily chlorinated in 20 per cent. hydrochloric acid when treated with three molecular proportions of chlorine in the same solvent. 2·85 Grams of the aniline were dissolved in 400 c.c. of 20 per cent. hydrochloric acid, and 315 c.c. of a 0·33*N*-solution of chlorine in the same medium were slowly run in whilst the mixture was vigorously stirred. The product which was precipitated by water was slightly coloured, and was purified by crystallisation, first from petroleum and then from 75 per cent. alcohol, from which it was obtained in long, colourless needles melting at 85°:

0·198 gave 0·4458 AgCl + AgBr. Cl + Br = 67·3.

$C_6H_3NCl_3Br$ requires Cl + Br = 67·65 per cent.

The *monoacetyl* derivative was prepared by heating a solution of the aniline in glacial acetic acid with a slight excess of acetyl chloride. It is somewhat readily soluble in alcohol or acetic acid, and is best recrystallised from benzene, from which solvent it separates in plates melting at 188—189°:

0·1696 gave 0·3292 AgCl + AgBr. Cl + Br = 58·50.

$C_8H_5ONCl_3Br$ requires Cl + Br = 58 7 per cent.

The *diacetyl* derivative is formed when the aniline is boiled with acetic anhydride for several hours. It crystallises from petroleum in short prisms melting at 133°–134°, and is readily soluble in the usual solvents:

0·1073 gave 0·1842 AgCl + AgBr. Cl + Br = 51·75.

$C_{10}H_7O_2NCl_3Br$ requires Cl + Br = 51·84 per cent.

Chlorination of 2 : 4-*Dichloroaniline.*

The production of *s*-trichloroaniline by chlorination of 2 : 4-dichloroaniline in hydrochloric acid is readily effected, but owing to the solubility of the trichloroaniline in water, the yield is small. Two grams of the dichloroaniline, which were dissolved in 200 c.c. of 20 per cent. hydrochloric acid and treated with 85·3 c.c. of 0·32*N*-solution of chlorine in the same medium, yielded only 0·91 gram of *s*-trichloroaniline on precipitation with water. The latter was, however, quite pure.

Chlorination of Sulphanilic Acid.

It was thought that possibly sulphanilic acid would yield a dichloro-derivative if it were chlorinated in hydrochloric acid solution. It was found, however, that even when 2 gram-molecules of chlorine were used, only *s*-trichloroaniline was formed, the remainder of the sulphanilic acid being unchanged.

Preparation of 2 : 4-*Dichloroacetanilide.*

The chlorination of acetanilide is not a difficult process, but to obtain a good yield of the 2 : 4-dichloro-derivative it is necessary to take many precautions. The following procedure has been found very successful. One hundred grams of acetanilide are dissolved in 800 c.c. of glacial acetic acid and 2 molecular proportions (131 grams) of powdered fused sodium acetate added. The flask and its contents are tared, and chlorine passed into the cold mixture. As soon as the *p*-chloroacetanilide crystallises out, the flask is heated on the water-bath and the passage of chlorine continued until weighing of the flask shows that 2 gram-molecules of chlorine have been absorbed. A slight excess of chlorine is often unavoidably used; this excess converts some of the dichloroacetanilide into the corresponding chloroamine, $C_6H_4Cl_2 \cdot NClAc$; hence it is advisable to add a few c.c. of a concentrated solution of sulphurous acid, which reconverts the chloroamine into anilide. The solid, which separates on cooling, consists of 2 : 4-dichloroacetanilide and sodium chloride, and is collected and freed from the latter by digestion with water.

The mother liquor can either be used for the chlorination of a further quantity of acetanilide, or it can be diluted with half its volume of warm water, when the remainder of the dichloroacetanilide crystallises out. The yield is theoretical.

Preparation of Acetylchloroamino-2:4-dichlorobenzene.—When acetylchloroamino-2 : 4-dichlorobenzene is used as a chlorinating agent for anilines, the following method of preparation has been found most convenient. The dichloroacetanilide, 50 grams, is dissolved in 500 c.c. of glacial acetic acid, and a solution of bleaching powder slowly added in sufficient quantity to give 5 per cent. excess of the calculated amount of chlorine. The bleaching powder should be as concentrated as possible; a 0·6—0·7*N*-solution is a suitable strength. If a more dilute solution is used, a larger volume of glacial acetic acid should be employed as solvent in order to avoid precipitation of the anilide when the solvent is diluted during the addition of the bleaching powder. After the chlorination is complete, cautious addition of water will cause the chloroamine to crystallise out. It is collected, washed with water, and dried over sulphuric acid and potassium hydroxide. Such a preparation has been found to contain 14·38—14·4 per cent. of chlorine attached to nitrogen, and therefore available for chlorinating the aniline, whilst the pure chloroamine contains 14·87 per cent.

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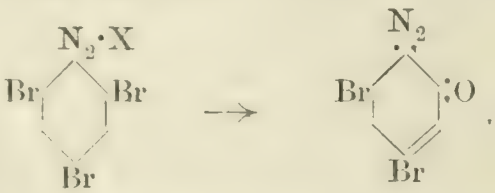
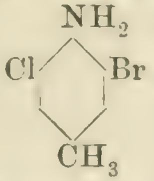
CXLVIII.—*Isomeric Change in Benzene Derivatives. Replacement of Halogen by Hydroxyl in Chlorobromodiazobenzenes.*

By KENNEDY JOSEPH PREVITÉ ORTON and WALTER WILLIAM REED.

IN earlier papers on this subject (Orton, *Proc. Roy. Soc.*, 1902, **71**, 153; Proc., 1902, **18**, 252; Trans., 1903, **86**, 796; *ibid.*, 1905, **87**, 99) the conditions influencing the elimination of halogen from chloro- or bromo-diazo-benzenes and -naphthalenes and the formation of quinonediazides have been studied:



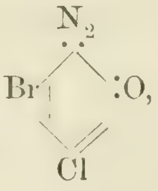
The investigation of mixed chlorobromodiazobenzenes seemed to be of particular interest and likely to throw light on the mechanism of this peculiar change. For this purpose, we chose the four symmetrical chlorobromoanilines, 2 : 6-dichloro-4-bromo- and 2 : 4-dichloro-6-bromo-anilines and the 2-chloro-4 : 6-dibromo- and 4-chloro-2 : 6-dibromo-anilines, and have also prepared the symmetrical 3-*chloro*-5-*bromo*-p-*toluidine*,  , hitherto undescribed, in which the para-position is occupied by a neutral group in so far as this reaction is concerned. In these compounds, the elimination of the halogen from the ortho- or para-positions will be free from the disturbing influences of asymmetry or the contiguity of other groups, for example, a nitro-group or halogen in the meta-position with respect to the diazo-group.

The change was followed under the same conditions, as were previously used (*loc. cit.*), with the diazonium acetates and bicarbonates. The solutions of these salts (1 per cent.) were prepared from the pure solid diazonium hydrogen sulphate, which was treated in aqueous solution with four equivalents of sodium acetate or bicarbonate. Two equivalents of these salts are required to replace the two equivalents of the strong acid, whilst a third equivalent similarly replaces hydrochloric and hydrobromic acids, which appear during the change, and would otherwise bring the reaction to a stop.

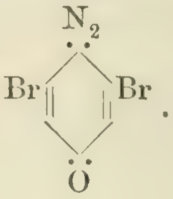
When the reaction ceases, some 60—65 per cent. of one atomic proportion of halogen is found in the ionic condition if sodium acetate, and about 80—90 per cent. if sodium bicarbonate, is used. In other words, of 100 molecules of the diazonium salt originally present, 60—65 molecules and 80—90 molecules respectively are converted into quinonediazide, at least in the first instance. As no diazonium salt is left undecomposed, the remainder (40 and 15 per cent.) undergoes changes, not accompanied by the elimination of halogen, which probably result in the formation of the yellow, amorphous substances of high molecular weight, which are constant products of the reaction.

In the first place, the investigation has demonstrated that in the decomposition of the *s*-trihalogenbenzenediazonium hydroxides the halogen is not only displaced by hydroxyl from the ortho-position relative to the diazo-group, but also from the para-position. The displacement from the para-position is subsidiary, but it is very easily recognised in the case of 2 : 6-dichloro-4-bromo- and 4-chloro-2 : 6-dibromo-diazobenzene ; bromidion is produced in the decomposition of the former and chloridion in that of the latter. For 100 molecules of the dichlorobromobenzenediazonium bicarbonate * which lose an atom of halogen, approximately 80 lose an atom of chlorine from one of the ortho-positions and 20 an atom of bromine from the para-position. (The mean value of the ratio of six experiments is 80·7 : 19·3.) The chlorodibromodiazobenzene loses halogen in the same proportion; 80 per cent. of the molecules which yield quinonediazide lose an atom of bromine from one of the ortho-positions, and 20 per cent. lose chlorine from the para-position.

This displacement of the *p*-halogen atom leads to the formation of the corresponding *p*-quinonediazide, which in the decomposition of the diazonium acetate is obtained mixed with the *o*-quinonediazide; thus 4-chloro-2 : 6-dibromodiazobenzene yields a mixture of 5-chloro-3-bromo-*o*-quinonediazide (I) and 3 : 5-dibromo-*p*-quinonediazide (II).

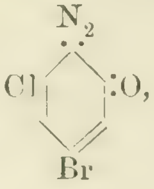


(I.)

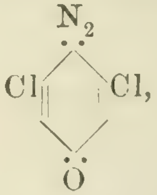


(II.)

Attempts at separation by use of solvents were unsuccessful. In the case of 2 : 6-dichloro-4-bromodiazobenzene, although the two corresponding quinonediazides are both formed, the crystalline separation consists wholly of the 3-chloro-5-bromo-*o*-quinonediazide (III), owing



(III.)



(IV.)

to the solubility of the 3 : 5-dichloro-*p*-quinonediazide (IV) and also to the small proportion in which it is produced.

In consequence of this discovery, a preliminary attempt was made to demonstrate the presence of 3 : 5-dibromo-*p*-quinonediazide among the products of the decomposition of *s*-tribromodiazobenzene (Orton, *loc. cit.*) by use of the greater solubility of the *o*-quinonediazide in alcohol, but without success. It is to be noted that only the *o*-quinonediazide was recognised by Bamberger (*Ber.*, 1906, **39**, 4248) in his investigation of the products of the action of alkali hydroxide on *s*-tribromobenzenediazonium nitrate.

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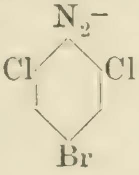
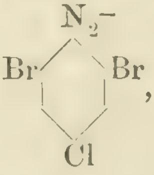
* The decompositions of the bicarbonates have been alone regarded in making these deductions, as the exceeding slowness of the change in the presence of acetic acid not only requires a great expenditure of time, but affords opportunity of subsidiary reactions, which may transfigure the result

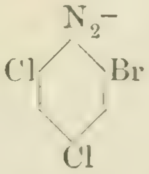
Examination of the results of our experiments leads to a second deduction. When chlorine and bromine are placed in similar positions in the benzene ring of the diazobenzenes and are similarly related to other substituents, there is little, if any, preference in the replacement of either by hydroxyl. The elimination appears to be independent of the nature of the halogen. This fact is obvious from the results stated in the foregoing with reference to 2 : 6-dichloro-4-bromodiazobenzene and 4-chloro-2 : 6-dibromodiazobenzene. A glance at the formulæ, 

and 

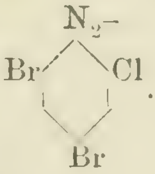
, shows that, on the one hand, the two atoms of chlorine (ortho) in the first are placed similarly to the two atoms of bromine in the second, and, on the other hand, that a para-placed atom of bromine in the one corresponds to the atom of chlorine in the other.

Of 100 molecules of the dichlorobromodiazo-compound, 80 lose one atom of chlorine from the ortho-positions and 20 lose one atom of bromine from the para-position. Of 100 molecules of the chlorodibromodiazo-compound, 80 lose one atom of bromine from the ortho-positions and 20 one atom of chlorine from the para-position, in other words, the atomic ratio, Cl : Br, from $C_6H_2Cl_2Br{\cdot}N_2-$ = the atomic ratio, Br : Cl, from $C_6H_2ClBr_2{\cdot}N_2-$ = 4 : 1.

Exactly similar evidence can be deduced from a consideration of the numbers observed in the decomposition of the two compounds, 2 : 4-dichloro-6-bromo- and 6-chloro-2 : 4-dibromo-diazobenzene :



and



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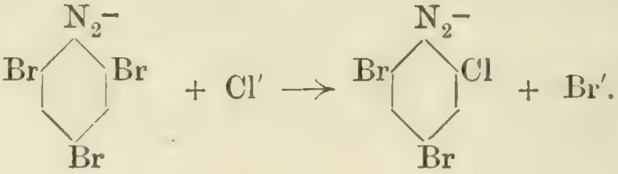
The atomic ratio, Cl : Br, from $C_6H_2Cl_2Br{\cdot}N_2-$ = the atomic ratio, Br : Cl, from $C_6H_2ClBr_2{\cdot}N_2-$ = 3 : 2 (approximately). Or, of 100 molecules of the dichlorobromodiazo-compound, 60 molecules lose one atom of chlorine and 40 lose one atom of bromine. The converse holds for the chlorodibromodiazo-compound.

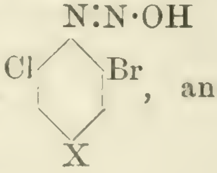
A further deduction can be made from a consideration of the analytical results obtained in the decomposition of these four chlorobromodiazobenzenes. Eighty per cent. of the halogen eliminated comes from the two ortho-positions, and, moreover, in equal amount from each position, whilst 20 per cent. is from the para-position. The ratio in which the three positions, 2, 4, 6, relative to the diazo-group, lose halogen, is then, approximately, 2 : 1 : 2.

In the hope of eliciting more direct evidence on this point, 3-chloro-5-bromo-*p*-diazotoluene was prepared, in which the para-position is occupied by a neutral group. But this diazo-compound, when in solution as a salt of a weak acid, loses but very little halogen. Although halogen is eliminated when the solutions of the diazotates are treated with acid, the major portion of the diazo-compound changes in other ways, and yields accordingly quantities of silver halide (generally less than 0·1 gram for 0·5 gram of diazonium salt) which do not permit of very certain analysis. Notwithstanding these difficulties, the atomic ratio of the chlorine and bromine is approximately = 1 : 1 (23 : 27). The bromine, it is true, is always found in slight excess, but it must be remembered that the constant error of the method of analysis, namely, the volatilisation of the silver halide during reduction in hydrogen, always tends to cause the percentage of bromine to appear high.

It was thought that the results of these experiments might be vitiated by a replacement of bromine by chloridion in the undecomposed diazonium salt, a reaction discovered by Hantzsch (*Ber.*, 1896, **29**, 947; 1897, **30**, 2337; 1900, **33**, 505), thus:



This supposition was tested* by allowing *s*-tribromobenzenediazonium acetate (a 1 per cent. solution) to decompose in a 10 per cent. solution of sodium chloride and then isolating and analysing the quinonediazide. The latter was found to contain no chlorine, but to be pure dibromoquinonediazide; hence the replacement of bromine by chloridion cannot take place to any considerable extent.

The interpretation of these results offers considerable difficulty. If the reaction consists merely in the elimination of halogen acid from diazo-hydroxide, , and subsequent rearrangement to the

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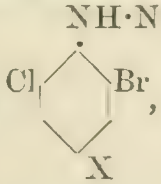
* 2·5 Grams (1 gram-molecule) of *s*-tribromobenzenediazonium hydrogen sulphate were dissolved in 150 c.c. of 16 per cent. sodium chloride to which 2·32 grams (3 gram-molecules) of crystallised sodium acetate dissolved in 100 c.c. of water were added. The mixture was kept for 28 days and the quinonediazide collected and freed from the yellow, amorphous material by shaking with water. It formed the usual orange, prismatic crystals melting and decomposing at 130°:

0·1602 gave 0·2165 AgCl + AgBr and 0·1246 Ag. Cl = 0·0; Br = 57·53.

$C_6H_2ON_2Br_2$ requires Br = 57·54 per cent.

quinonoid structure, some more distinct preferential formation of hydrogen chloride or hydrogen bromide than we have observed would seem probable. Although little systematic study on the relative ease of replacement of chlorine and bromine from benzene derivatives appears to have been made, there is little doubt that considerable difference between these two halogens exists. For example, Luloffs (*Rec. trav. chim.*, 1901, **20**, 292), in a comparative study of the action of sodium ethoxide on the 1-halogen-2 : 4-dinitrobenzenes, found that chlorine was displaced twice as rapidly as bromine.

The same objections * may be urged against Hantzsch's view (*Ber.*, 1903, **36**, 2069), that the halogen acid is eliminated from a primary nitrosoamine, 

, which is formed by molecular rearrangement of the diazo-hydroxide.

But apart from the fact that there is no preferential elimination of either halogen, all chemical experience tends to show that halogen is not eliminated as halogen acid or directly replaced by hydroxyl from a *s*-trihalogen benzenoid compound of this type, under the conditions described above.

In previous papers, it has been urged that the reaction is far less simple and is the result of a series of molecular rearrangements involving the structure of the benzene nucleus.† Thus it was suggested that the benzenediazo-hydroxide (or diazonium hydroxide) (I) passes into a quinonoid complex (II and II*a*) (in fact, a "carbonium" salt), in which process the hydroxyl group has of necessity migrated to a carbon atom of the nucleus:

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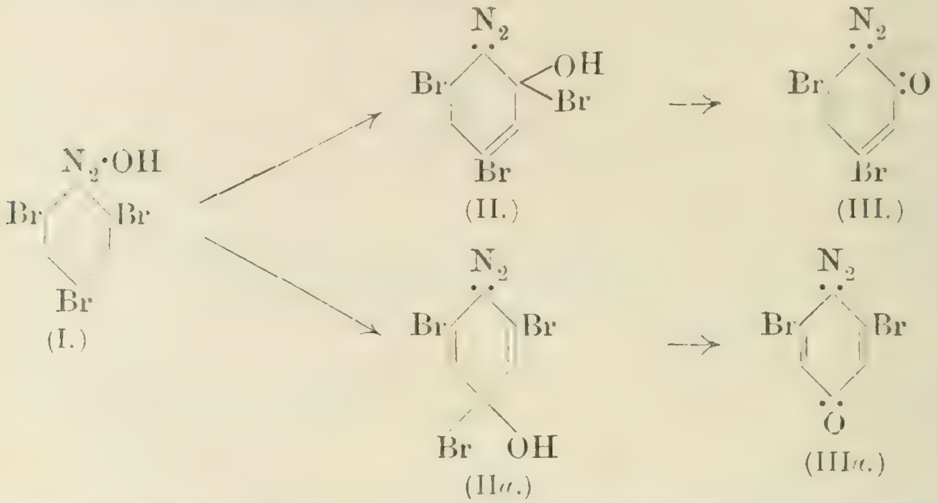
* The formation of nitrosoamines, Ar·NH·NO, from *s*-trihalogendiazobenzenes, under the conditions, when halogen is eliminated, that is, in faintly acid or faintly alkaline solution (Orton, *loc. cit.*), has been maintained by Hantzsch (*loc. cit.*). Although he no longer states, as was originally the case (Hantzsch and Pohl, *Ber.*, 1902, **35**, 2964), that the nitrosoamine is the sole product of this reaction, but at most is a minor constituent of a mixture which consists mainly of dibromoquinonediazide and an amorphous substance of high molecular weight, he has not publicly replied to the demonstration, given by one of us (Orton, Trans., 1905, **87**, 99), that the evidence on which he finally relied, of the existence of the nitrosoamine in the solid product of the decomposition, is not forthcoming. This evidence is mainly based on the formation of *s*-tribromobenzeneazo-β-naphthol when the alcoholic extract of the solid product is treated with β-naphthol. In correspondence, Prof. Hantzsch has admitted that on this test the decision as to the existence of the nitrosoamine in the mixture should rest. In our experience, however, when the solid product is freed from unchanged diazonium salt (which will, of course, couple with the β-naphthol), this tribromobenzeneazo-β-naphthol can never be isolated.

† The conversion of nitrodiazobenzenes into quinonediazides with loss of a nitro-group, first observed by Griess, but fully studied by Meldola (Proc., 1896, **14**, 226 ; *et seq.*), appears to be a change of the same type. In particular, it may be noted that a recent observation by Meldola (Trans., 1905, **87**, 1199) is in agreement with the hypothesis sketched above. When dinitro-*o*-anisidine is diazotised in



These complexes may lose halogen acid directly, or possibly again return to a benzenoid configuration, the halogen, however, and not the hydroxyl moving on this occasion; finally, in any case, a quinonediazide (III and III*a*) is produced.*

The facts recorded herein are readily represented in terms of this hypothesis. As long as the orientation of the benzene nucleus is symmetrical, there can be no preference for either of the *o*-quinonoid phases. (For the moment we may disregard the relation to the simultaneous formation of a *p*-quinonoid phase.) Moreover, the effect of the difference of the halogen with two such similar atoms, in the ortho-position, on the symmetry can be but slight. Hence in the transformation of the benzenoid to the quinonoid phases, the frequency of formation of the two ortho-phases may be taken as nearly equal. The chlorine and bromine would then be eliminated from the ortho-positions in atomic proportions.

From the numbers given in the foregoing, it is possible to deduce approximately the relative frequencies of occurrence of the *o*- and *p*-quinonoid phases in these symmetrical compounds. Each *o*-quinonoid phase is formed *twice* as often, or, in all, an *o*-quinonoid phase *four* times as often as the *p*-quinonoid phase.

Hantzsch's observations, previously referred to, are in agreement with our conclusions. Thus he found by comparison of 2 : 6-dibromodiazobenzene with 2 : 4-dibromodiazobenzene and of 2 : 6-dibromo-*p*-di-

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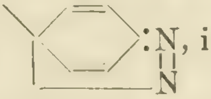
acetic acid solution, a nitro-group is eliminated, but the diazotisation is not accompanied by such a change if carried out in sulphuric acid.

* This process was regarded (*loc. cit.*) as analogous to that which takes place in conversion of nitroamines, &c., into the isomeric nitroanilines.

azotoluene with 2 : 4-dibromo-*o*-diazotoluene that the *o*-bromine was replaced by chlorine with considerably greater velocity than the *p*-bromine. His figures do not lend themselves to any approximate calculation of the ratio, but this similarity obviously points to the replacement of bromine by chlorine and our replacement of halogen by hydroxyl being kindred processes.

Attention must be drawn to the contrast which the molecular rearrangement of derivatives of anilines (in which one atom or group "wanders" from the amino-group into the nucleus) offers to the transformation of diazo-compounds here considered. It is true that occasionally the migrating group takes up mainly the ortho-position with respect to the amino-group, as in the transformation of nitroaminobenzene to *o*-nitroaniline. More generally, however, the wandering group enters mainly the para-position when the benzene nucleus is symmetrically constituted. Not only is this shown in the chlorination and bromination of aniline and acetanilide, but also in a remarkable manner in the displacement of bromine by the nitro-group in *s*-tribromoaniline (Orton, Trans., 1902, **81**, 490) and of bromine by chlorine, a reaction which is described in the preceding paper (this vol., p. 1543).

These results have some bearing on Cain's (this vol., p. 1049) recent suggestions, that diazo-compounds are better represented as of bicyclic quinonoid structure,  instead of as benzenoid derivatives. Apart from any objections which may be raised, on the ground of the general chemical behaviour of this class, to the linking of the diazo-group to *two* carbon atoms of the nucleus, Cain's formulation does not permit (if our hypothesis as to the mechanism of the reaction be valid) of any ready representation of the remarkable fact that the elimination of the halogen from the three positions (2, 4, and 6) is in a fixed ratio, unless we assume that in solution his single *p*-quinonoid bicyclic structure is not preserved, but alternates with two similar *o*-quinonoid phases. Moreover, even with that assumption, this formulation does not help in accounting for the transference of the group (halogen, hydroxyl, &c.) from the nitrogen of the diazo-group to the carbon of the nucleus.

On the authors' view, on the other hand, the solid diazonium salts possess a benzenoid structure, but in solution may be partly transformed, probably only to a very small extent, into the three quinonoid phases, in which the group linked to the diazo-nitrogen becomes associated with the carbon. In certain contingencies, when the atom or group already linked with the carbon can interchange functions with the migrating radicle, this quinonoid phase may undergo further transformations.

EXPERIMENTAL.

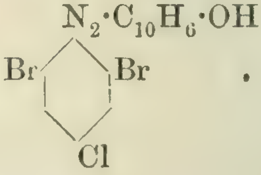
Experiments with 4-*Chloro*-2 : 6-*dibromodiazobenzene.*

The 4-chloro-2 : 6-dibromoaniline required for these experiments was prepared from 4-chloroaniline, which had been obtained from a pure specimen of 4-chloroacetanilide, and melted at 68—68·5°. The bromination was carried out in glacial acetic acid, and the chlorodibromoaniline, which crystallised in long, colourless needles, melted at 95·5°.

4-*Chloro*-2 : 6-*dibromobenzenediazonium Hydrogen Sulphate.*

This salt was prepared in the usual manner. Ten grams of the aniline were dissolved in 25 c.c. of glacial acetic acid and a solution of 2·5 c.c. of concentrated sulphuric acid in 25 c.c. of glacial acetic acid (that is, rather more than 1 gram-molecule) added. 5·5 c.c. of amyl nitrite (1¼ gram-molecule) were then slowly run in, the mixture being kept stirred by the turbine. Cautious addition of ether caused the diazonium salt to crystallise out; it was collected, washed with ether, and dried between filter paper, 11·5 grams being obtained.

4-*Chloro*-2 : 6-*dibromobenzene*-1-*azo*-β-*naphthol,*



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The ordinary methods of coupling diazo-compounds with β-naphthol in alkaline solutions are not applicable to the *s*-trihalogendiazobenzenes, as halogen is readily eliminated in mixing the solution of the diazo-salt with the alkaline solution of β-naphthol (Orton, Trans., 1903, **83**, 807). The following method, however, gives very satisfactory results and a quantitative yield. 0·5 Gram of the diazonium hydrogen sulphate is dissolved in 95 per cent. alcohol and a solution of a slight excess of β-naphthol in 50 c.c. alcohol added. Coupling is rapid, the azo-compound separating out in scarlet crystals. It is best recrystallised from glacial acetic acid containing a little acetic anhydride, from which medium it separates in silky, scarlet needles melting at 156—157°:

0·1827 gave 0·2139 AgCl + AgBr and 0·1336 Ag. Cl = 8·14 ; Br = 35·81.

$C_{16}H_9ON_2ClBr_2$ requires Cl = 8·05 ; Br = 36·30 per cent.

Decomposition of 4-*Chloro*-2 : 6-*dibromobenzenediazonium Hydrogen Carbonate.*—The decomposition of the diazonium bicarbonate was studied in the following manner. A solution of 0·5 gram of diazonium hydrogen sulphate in 25 c.c. of distilled water was mixed with a solution of 0·32 gram of sodium bicarbonate (three equivalents) and the mixture kept at an equable temperature. Decomposition was complete in eighteen hours, no further change occurring, however, if the mixture was kept for a much longer period, as, for example, a week or ten days. On mixing, a yellow coloration immediately appeared and a precipitate began to form. The product of the reaction consisted of a yellow liquid and a precipitate which was obviously a yellow, amorphous material containing small, orange crystals; the latter consists of a mixture of quinonediazides.

The chlorine and bromine ions were estimated in the yellow filtrate in the following manner. The filtrate was received directly during the filtration into 20 c.c. of 10 per cent. nitric acid, further change being thus prevented. Silver nitrate was now added, and the precipitated silver chloride and bromide collected in Gooch crucibles. Owing to the fact that a certain amount of organic matter is carried down with the precipitate of silver halide, it was necessary to treat the silver halides as follows. The mother liquor was decanted through a weighed crucible and the precipitate washed free from the silver nitrate by decantation, the washings being passed through the crucible. The precipitate was then washed by decantation, twice with alcohol, twice with ether, again with alcohol, and finally with water, the washings all being passed through the crucible. It was occasionally found advisable to interpose a washing with benzene between the washing with ether. The precipitate, which was now completely free from organic matter, was collected in a second Gooch crucible. The former crucible did not contain more than one-sixth of the total precipitate. The proportion of chloride and bromide in the mixture of silver halides was generally determined by reduction of the silver halide to metallic silver by hydrogen, the Gooch being placed in a Rose crucible for the purpose. This procedure gives too high a value for the bromine, as there is always some loss in the reduction, due to volatilisation. The following numbers were obtained in two experiments, carried out as above, 0·5 gram of the diazonium hydrogen sulphate being used. The ratio Cl : Br is expressed in gram-atoms:

1. AgCl + AgBr = 0·2002; Ag = 0·1199; Cl = 8·45, and Br = 91·55 per cent. Cl : Br = 1 : 4·79.
2. AgCl + AgBr = 0·2002; Ag = 0·1199; Cl = 8·45, and Br = 91·55 per cent. Cl : Br = 1 : 4·79.
3. AgCl + AgBr = 0·2053; Ag = 0·1227; Cl = 8·00, and Br = 92·00 per cent. Cl : Br = 1 : 5·1.

Decomposition of 4-Chloro-2 : 6-dibromobenzenediazonium Acetate.— As the decomposition of the diazonium acetate is a much slower process than that of the bicarbonate, it is advisable to allow at least seven days before the mixture is analysed. We have generally let three weeks elapse.

Five grams of the diazonium hydrogen sulphate, dissolved in 250 c.c. of water, were mixed with a solution of 10·4 grams of crystallised sodium acetate (6 gram-molecules). The mixture was kept for twenty-three days. At the end of that period, a heavy precipitate, which consisted of orange crystals mixed with an amorphous, yellow powder, had formed. This solid was collected, and the filtrate received in 100 c.c. of 10 per cent. nitric acid. The chlorine and bromine ions were then estimated in the filtrate in the manner previously described:

1. AgCl + AgBr = 0·2136 ; Ag = 0·1293 ; Cl = 10·8, and Br = 89·2 per cent. Cl : Br = 1 : 3·66.
2. AgCl + AgBr = 0·2162 ; Ag = 0·1308 ; Cl = 10·78, and Br = 89·22 per cent. Cl : Br = 1 : 3·67.
3. AgCl + AgBr = 0·1968 ; Ag = 0·1192 ; Cl = 10·64, and Br = 89·36 per cent. Cl : Br = 1 : 3·72.

It will be noted that the ratio of chlorine to bromine differs considerably from that found in the experiments with the bicarbonate.

The Quinonediazide.—The quinonediazide was separated from the amorphous, yellow solid by taking advantage of its greater density. The mixture was suspended in water and, after vigorously stirring, the liquor decanted, when the amorphous material was poured off with the water, leaving the quinonediazide in the flask. Repetition of this process sufficed to separate the quinonediazide completely from the other substance. The quinonediazide was apparently homogeneous, and consisted of orange-yellow crystals melting and decomposing at 165°. Analysis showed, however, that the quinonediazide was a mixture probably of 3-chloro-5-bromoquinone-6-diazide and 3 : 5-dibromoquinone-4-diazide:

0·1562 gave 0·2196 AgCl + AgBr and 0·1391 Ag. Cl = 11·53 ; Br = 40·01 per cent.

0·2017 gave 0·2835 AgCl + AgBr and 0·1791 Ag. Cl = 11·1 ; Br = 40·6 per cent.

Assuming that only the two quinonediazides just mentioned are present, the mixture consists of 74·7 per cent. of the chlorobromo- and 25·3 of the dibromo-quinonediazide, that is, 77 gram-molecules of the chlorobromo- to 23 gram-molecules of the dibromo-quinonediazide. The proportion of the dibromoquinonediazide is greater than that demanded by the relative amounts of chlorine and bromine ions discovered in the filtrate; the discrepancy is probably accounted for by the greater solubility of the chlorobromo-*o*-quinonediazide.

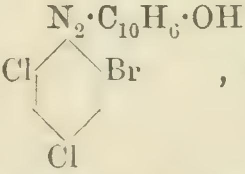
These results were confirmed by converting the quinonediazide into the β-naphthol derivative by the method previously described in an earlier paper (Trans., 1905, **87**, 104). 0·2 Gram of the orange prisms, dissolved in 40 c.c. methyl alcohol, was mixed with a slight excess of β-naphthol in the same solvent. 0·2 c.c. of a 1 per cent. solution of sodium hydroxide was introduced, whereupon coupling took place, an intense coloration appearing. Within a few minutes, crystals, melting at 195—203°, separated. Analysis showed that some dibromo-*p*-hydroxybenzeneazo-β-naphthol, $OH{\cdot}C_6H_2Br_2N_2{\cdot}C_{10}H_6{\cdot}OH$, was present:

0·2275 gave 0·2001 AgCl + AgBr and 0·1282 Ag. Cl = 8·07; Br = 23·54.
$C_{16}H_{10}O_2N_2ClBr$ requires Cl = 9·38; Br = 21·13 per cent.

Experiments with 2 : 4-*Dichloro*-6-*bromodiazobenzene.*

The starting point of the preparation of 2 : 4-dichloro-6-bromoaniline was 2 : 4-dichloroacetanilide, which was obtained in a very pure condition (see this vol., p. 1553). The anilide was hydrolysed and the 2 : 4-dichloroaniline brominated in acetic acid. The resulting aniline was recrystallised from alcohol and melted at 81·5—82°.

2 : 4-*Dichloro*-6-*bromobenzenediazonium hydrogen sulphate* was easily prepared in the manner given above.

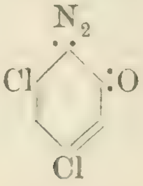
2 : 4-*Dichloro*-6-*bromobenzene*-1-*azo*-β-*naphthol*, 
$N_2{\cdot}C_{10}H_6{\cdot}OH$, Cl, Br, Cl
, was prepared from the diazonium sulphate and β-naphthol in methyl-alcoholic solution. It crystallised from acetic acid containing acetic anhydride in scarlet, silky needles melting at 148—149°:

0·1866 gave 0·2242 AgCl + AgBr and 0·153 Ag. Cl = 17·99; Br = 20·16.
$C_{16}H_9ON_2Cl_2Br$ requires Cl = 17·90; Br = 20·19 per cent.

Decomposition of the 2 : 4-*Dichloro*-6-*bromobenzenediazonium Hydrogen Carbonate.*—The decomposition of the hydrogen carbonate was followed in a manner exactly similar to that described in the foregoing. In this case, no orange crystals were mixed with the amorphous precipitate; in other respects, the change was quite similar:

1. AgCl + AgBr = 0·1969; Ag = 0·1311; Cl = 37·93; Br = 62·07 per cent. Cl : Br = 1 : 0·72.
2. AgCl + AgBr = 0·2105; Ag = 0·1402; Cl = 38·02; Br = 61·88 per cent. Cl : Br = 1 : 0·72.

Decomposition of the 2 : 4-*Dichloro*-6-*bromobenzenediazonium Acetate.*—The reaction was carried on as before, a 1 per cent. solution of the diazonium salt being used. The solution of the acetate was only kept for one week, and hence only a small proportion of the diazonium salt had decomposed. Partly on account of the short duration of the experiment and partly owing to the fact that three quinonediazides are formed, one of which, the 3 : 5-dichloroquinonediazide, is easily soluble in water (*Proc. Roy. Soc.*, 1902, **71**, 157), no orange crystals separate with the amorphous powder. The three quinonediazides, which may possibly be produced, are the 3 : 5-dichloro- (I)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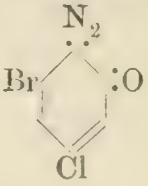
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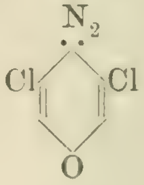

(III.)

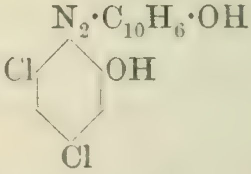
and 3-chloro-5-bromo-*o*-quinonediazide (II), and the 3 : 5-dichloro-*p*-quinonediazide (III). After filtering off the yellow, amorphous solid, the quinonediazides were extracted from the yellow, aqueous filtrate by means of chloroform. On evaporating the chloroform, a crystalline residue remained, which was dissolved in methyl alcohol, and coupled with β-naphthol in the presence of a trace of alkali in order to obtain the quinonediazides in a form the analysis of which would be more trustworthy. The coupled product was crystalline, 2·4 grams being obtained from the 5 grams of diazonium hydrogen sulphate. The material had an indefinite melting point, 195—205°, and its analysis indicated that it was a mixture of dichlorohydroxybenzeneazo- and chlorobromohydroxybenzeneazo- (possibly two) β-naphthol:

0·1404 gave 0·1213 AgCl + AgBr and 0·0832 Ag. Cl = 17·13; Br = 9·30.

$C_{16}H_{10}O_2N_2Cl_2$ requires Cl = 21·29 per cent.

$C_{16}H_{10}O_2N_2ClBr$ requires Cl = 9·39; Br = 21·18 per cent.

Hence the mixture contains 65·4 per cent. of a dichloro-derivative.

3 : 5-Dichloro-1-hydroxybenzene-2-azo-β-naphthol,* 

—This derivative of 3 : 5-dichloroquinone-*o*-diazide, which has not hitherto been prepared, was obtained as follows. Two grams of *s*-trichlorobenzenediazonium hydrogen sulphate were dissolved in 200 c.c. of water containing three equivalents of sodium acetate, and the mixture kept for one week. The amorphous material and the bright yellow mother liquor were extracted with chloroform three times. The crystalline residue, which consisted of 3 : 5-dichloroquinone-*o*-diazide, left on evaporating the chloroform, was dissolved in 75 c.c. of alcohol, and a slight excess of β-naphthol dissolved in alcohol added. On making alkaline with 1 c.c. of 1 per cent. sodium hydroxide, coupling began, and scarlet needles separated. After being recrystallised from alcohol, these melted at 205°:

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* For the preparation and analysis of this substance, we have to thank Mr. E. Towyn Jones, B.Sc.

0·1132 gave 0·0972 AgCl. Cl = 21·22.

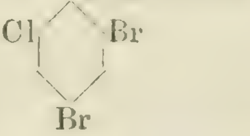
$C_{16}H_{10}O_2N_2Cl_2$ requires Cl = 21·29 per cent.

Experiments with 2-*Chloro*-4 : 6-*dibromodiazobenzene.*

The starting point of this diazo-compound was *p*-bromoacetanilide. This compound is converted into the corresponding chloroamine, which then changes into the isomeric 2-chloro-4-bromoacetanilide; the aniline corresponding to the latter is then directly brominated in acetic acid solution, 2-chloro-4 : 6-dibromoacetaniline being produced. For the reasons given in the preceding paper (this vol., p. 1545), the chlorodibromoaniline cannot be obtained in a pure state by chlorinating 2 : 4-dibromoaniline.

p-Bromoacetanilide can be converted into the chloroamine in various ways; the following procedure has been found convenient when, not the pure chloroamine, but the isomeric chlorobromoacetanilide is desired. The *p*-bromoacetanilide in a very finely divided condition is suspended in *N*/2 bleaching powder solution, the latter being in slight excess (5 per cent.) of the calculated amount. The mixture is vigorously stirred by means of the turbine, or shaken in a flask, dilute acetic acid being added from time to time in small quantities. The chlorination is slow, but the anilide is, finally, nearly completely converted into the chloroamine. The product is collected and dissolved in glacial acetic acid containing 1 or 2 c.c. of concentrated hydrochloric acid. On standing, 2-chloro-4-bromoacetanilide crystallises out, and can be purified by one recrystallisation from alcohol, when it melts sharply at 151°.

2-*Chloro*-4 : 6-*dibromobenzenediazonium Hydrogen Sulphate.*—This salt is easily prepared in the usual manner from the corresponding aniline, which melted at 99°.

2-*Chloro*-4 : 6-*dibromobenzene*-1-*azo*-β-*naphthol*,  .—

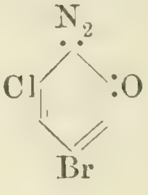
This compound was prepared from the diazonium salt and β-naphthol after the manner described in the foregoing. It crystallised from glacial acetic acid containing acetic anhydride in scarlet needles melting at 160--161°:

0·2164 gave 0·2532 AgCl + AgBr and 0·1580 Ag. Cl = 8·04; Br = 35·95.
$C_{10}H_9ON_2ClBr_2$ requires Cl = 8·05; Br = 36·30 per cent.

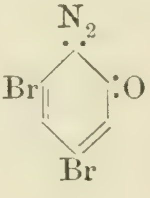
Decomposition of 2-*Chloro*-4 : 6-*dibromobenzenediazonium Hydrogen Carbonate*.—The decomposition was carried out exactly as described in the foregoing, with the following results:

1. AgCl + AgBr = 0·178; Ag = 0·1132; Cl = 23·40, and Br = 76·6 per cent. Cl : Br = 1 : 1·42.
2. AgCl + AgBr = 0·1500; Ag = 0·0960; Cl = 24·1, and Br = 75·9 per cent. Cl : Br = 1 : 1·41.

Decomposition of 2-*Chloro*-4 : 6-*dibromobenzenediazonium Acetate*.—Five grams of the diazonium hydrogen sulphate were treated with sodium acetate in dilute aqueous solution (1 per cent.) as described above, the mixture being kept for thirty-one days. A considerable quantity of orange crystals, quinonediazides, separated. In the case of this diazonium salt, three quinonediazides may be formed, two *o*-quinonediazides, 5-chloro-3-bromo-*o*-quinonediazide (I.), 3:5-dibromo-*o*-quinonediazide (II.), and 3-chloro-5-bromo-*p*-quinonediazide (III.):



(I.)



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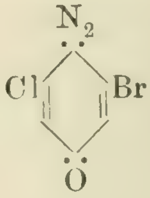


(III.)

As has been explained in the introduction, the *p*-derivative would be formed in only small proportion, but its sparing solubility would give it a disproportionately prominent place in the crystalline separation.

The quinonediazides were separated from the yellow, amorphous solid product of the reaction by following the same procedure as described under 4-chloro-2 : 6-dibromodiazobenzene. The crystals were apparently homogeneous, and, after drying over sulphuric acid, melted and decomposed at 128°. Analysis gave the following numbers:

0·1527 gave 0·2106 AgCl + AgBr and 0·1271 Ag. Cl = 5·57; Br = 49·12 per cent.
0·1521 gave 0·2122 AgCl + AgBr and 0·1277 Ag. Cl = 5·23; Br = 49·97 per cent.

From these results, it follows that the orange crystals contain 36 per cent. of the chlorobromo-*o*-quinonediazide and chlorobromo-*p*-quinonediazide, and 64 per cent. of the dibromo-*o*-quinonediazide.

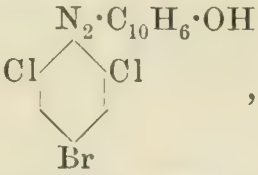
The greater solubility of the 3-chloro-5-bromo-*o*-quinonediazide would, however, considerably lessen its proportion in the crystalline separation.

The aqueous liquor from which the solid products of the decomposition had been separated was examined for chlorine and bromine ions. The proportion of gram-atoms of chlorine to gram-atoms of bromine was 44·2 : 55·8 for each 100 gram-molecules of diazonium salt which had decomposed. This proportion demonstrates with great emphasis the fact that the composition of the crystals of quinonediazides does not represent the proportions in which the different halogen atoms are eliminated.

Experiments with 2 : 6-*Dichloro*-4-*bromodiazobenzene.*

2 : 6-Dichloro-4-bromoaniline, which was prepared as described in the preceding paper (this vol., p. 1547), was converted into the corresponding diazonium hydrogen sulphate in the usual manner.

2 : 6-*Dichloro*-4-*bromobenzene*-1-*azo*-*β*-*naphthol*,



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was prepared from the diazonium salt and *β*-naphthol in methyl-alcoholic solution. It crystallised in silky, scarlet needles from acetic acid and acetic anhydride, and melted at 170° :

0·1773 gave 0·2128 AgCl + AgBr and 0·1452 Ag. Cl = 17·95; Br = 20·17.

$C_{16}H_9ON_2Cl_2Br$ requires Cl = 17·90 ; Br = 20·19 per cent.

Decomposition of 2 : 6-*Dichloro*-4-*bromobenzenediazonium Hydrogen Carbonate.*—The decomposition was carried out in the usual manner, the solution of the bicarbonate being kept for about seventy hours. The solid product of the reaction was a yellow, amorphous material. The yellow filtrate was examined for chloride and bromide as in the case of other similar decompositions :

I. AgCl + AgBr = 0·2095 ; AgCl = 0·1989 ; Cl = 68·17, and Br = 31·83 per cent. Br : Cl = 1 : 4·5.

Decomposition of the 2 : 6-*Dichloro*-4-*bromobenzenediazonium Acetate.*—In this decomposition, which was allowed to proceed for three weeks, a quantity of crystalline quinonediazide appeared ; the crystals were separated from the amorphous material in the usual manner, and, after drying over sulphuric acid, were found to melt at 115—116° and decompose at 118°. Analysis showed that the material was practically pure 3-*chloro*-5-*bromo*-o-*quinonediazide.* The smaller quantity of the more soluble 3 : 5-dichloro-*p*-quinonediazide which was produced remained in the solution ;

0·1558 gave 0·2196 AgCl + AgBr and 0·1898 AgCl. Cl = 14·89; Br = 34·36.

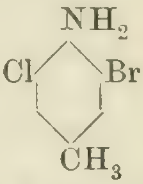
$C_6H_2ON_2ClBr$ requires Cl = 15·18; Br = 34·24 per cent.

Estimation of the chloride and bromide in the yellow filtrate showed that some 30 per cent. of bromine was eliminated, and consequently the same amount of 3 : 5-dichloro-*p*-quinonediazide had been produced.

*Experiments with 3-Chloro-5-bromo-*p*-diazotoluene.*

The starting point of this series of experiments was 3-chloro-*p*-toluidine, the preparation of which base presented considerable difficulty.

Aceto-*p*-toluidide was treated in glacial acetic acid with a small excess of bleaching powder solution. The oily product of the reaction was boiled with a known excess of 20 per cent. hydrochloric acid; when hydrolysis was complete, the hydrochloric acid was cautiously neutralised with sodium hydroxide, so that some hydrochloride of the base remained undecomposed. On distilling this mixture in steam, the more basic unchanged *p*-toluidine remained in the distilling flask, whilst the less basic 3-chlorotoluidine passed over. The latter was finally purified by conversion into its acetyl derivative, which was then recrystallised from dilute acetic acid.

3-*Chloro-5-bromo-*p*-toluidine*, .—This base, which has not up to the present been described, was readily prepared by adding a solution of 3-chlorotoluidine in glacial acetic acid to the equimolecular proportion of bromine in the same solvent. After the addition, the mixture was boiled until the major portion of the hydrogen bromide had been driven off. The *chlorobromotoluidine*, which separated on cooling, was recrystallised from alcohol; it forms colourless needles melting at 65°:

0·0944 gave 0·1418 AgCl + AgBr. AgCl + AgBr = 150·2.

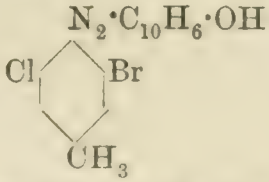
C_7H_7NClBr requires AgCl + AgBr = 150·3 per cent.

The *acetyl* derivative was obtained by treatment of the base in glacial acetic acid solution with acetyl chloride. It crystallised from alcohol in prisms melting at 189°:

0·1020 gave 0·1297 AgCl + AgBr and 0·0845 Ag. Cl = 13·59; Br = 30·68.

$C_9H_9ONClBr$ requires Cl = 13·51; Br = 30·46 per cent.

3-*Chloro-5-bromo-*p*-toluenediazonium hydrogen sulphate* is readily prepared from the chlorobromotoluidine.

*3-Chloro-5-bromo-*p*-tolueneazo-β-naphthol,** , was obtained by coupling the diazonium hydrogen sulphate with β-naphthol in ethyl-alcoholic solution. The hydroxyazo-compound separated directly in scarlet needles melting at 129—130°. It was recrystallised from acetic acid:

0·1612 gave 0·1426 AgCl + AgBr. AgCl + AgBr = 88·46.
$C_{17}H_{12}ON_2ClBr$ requires AgCl + AgBr = 88·15 per cent.

*Decomposition of 3-Chloro-5-bromo-*p*-toluenediazonium Hydrogen Carbonate.*—The decomposition of the bicarbonate, which was carried out in the same manner as previously described, did not give satisfactory results. It has been previously observed with the similarly constituted 3 : 5-dibromo-*p*-toluenediazonium hydrogen carbonate that, although decomposition of the diazo-compound is both rapid and complete, very little halogen is eliminated; the decomposition proceeds in other directions. Hence it was to be anticipated that with the compound under consideration, sufficient halogen would not be eliminated to allow of any accurate conclusion being drawn as to the relative amounts of chlorine and bromine.

*Decomposition of Sodium 3-Chloro-5-bromo-*p*-toluene Diazotate.*—A more complete elimination of halogen was obtained when a solution of the diazotate in excess of sodium hydroxide was treated with sufficient nitric acid to remove excess of alkali.

0·5 Gram of the diazonium hydrogen sulphate dissolved in 15 c.c. of water was added to 50 c.c. of a 1 per cent. solution of sodium hydroxide. The excess of sodium hydroxide was then removed by cautious addition of nitric acid; the liquid still possessed an alkaline reaction towards litmus; decomposition was rapid, a yellow, amorphous precipitate being formed. The estimation of the halogen as chloride and bromide was carried out by the method described in the foregoing; in this case, however, greater difficulty was experienced in freeing the silver halide from organic matter:

1. AgCl + AgBr = 0·0996; Ag = 0·0642; Cl = 27·36, and Br = 72·64 per cent. Cl : Br = 1 : 1·174.
2. AgCl + AgBr = 0·0975; Ag = 0·0629; Cl = 27·63, and Br = 72·37 per cent. Cl : Br = 1 : 1·16.
3. AgCl + AgBr = 0·0949; Ag = 0·0612; Cl = 27·57, and Br = 72·43 per cent. Cl : Br = 1 : 1·165.

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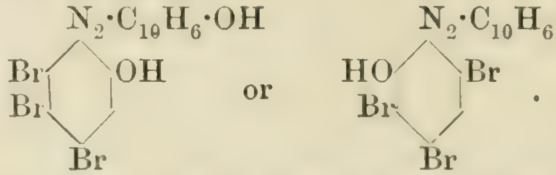
* For the preparation and analysis of this substance, we have to thank Mr. R. W. Everatt, B.Sc.

Tribromophenolazo-β-naphthol,[*]


$N_2 \cdot C_{10}H_6 \cdot OH$
Br
OH
Br
Br
or
$N_2 \cdot C_{10}H_6 \cdot OH$
HO
Br
Br
Br

—Since the two bromine atoms in the ortho-position in the tetrabromobenzenediazonium salts do not bear the same relation to the rest of the molecule, a mixture of two isomeric quinonediazides, namely, 2 : 3 : 5-tribromo- and 3 : 4 : 5-tribromo-quinonediazide, may be formed (and possibly a third, 2 : 5 : 6-tribromo-*p*-quinonediazide). The product obtained in the decomposition of the acetate does not show any signs of being a mixture (Trans., 1903, **83**, 811), but when coupled with *β*-naphthol the product, which crystallises in scarlet needles, shows a melting point of 203°, which can be raised to 212—216° by repeated crystallisation from acetic acid containing acetic anhydride :

0·0685 gave 0·0764 AgBr. Br = 47·5.

$C_{16}H_9O_2N_2Br_3$ requires Br = 47·9 per cent.

Tetrabromobenzeneazo-β-naphthol, $C_6HBr_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, crystallises from acetic acid containing acetic anhydride in scarlet needles melting at 205—207°.

The authors wish to take this opportunity of acknowledging their indebtedness to the Recommendations Committee of the British Association for the grant which has partly defrayed the cost of this enquiry.

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BANGOR

CXLIX.—*The Relation between Absorption Spectra and Chemical Constitution. Part VIII. The Phenylhydrazones and Osazones of a-Diketones.*

By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, EFFIE GWENDOLINE MARSDEN, and (in part) MAUD GAZDAR.

THE results described in this paper are in continuation of those dealt with in a previous communication (Baly and Tuck, Trans., 1906, **89**, 982) on the phenylhydrazones of simple aldehydes and ketones. We have extended the same methods of investigation to the compounds of phenylhydrazine with certain α-diketones with the view of determining their constitution, and by a comparison of the absorption spectra of the phenylhydrazones and osazones with those of the corresponding phenylmethyl compounds we have been led to the conclusion that the constitution must be that usually assigned, namely:

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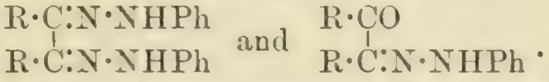
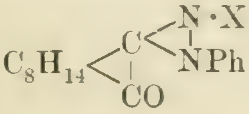
[*] For the preparation and analysis of these substances, the authors have to thank Mr. J. E. Coates, B.Sc.

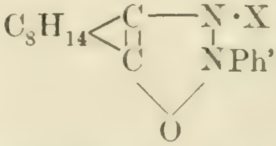


$$\begin{matrix} R\cdot C\colon N\cdot NHPh \\ | \\ R\cdot C\colon N\cdot NHPh \end{matrix} \quad \text{and} \quad \begin{matrix} R\cdot CO \\ | \\ R\cdot C\colon N\cdot NHPh \end{matrix}\ .$$

Armstrong and Robertson, in their paper on "Optical Properties as Connoting Chemical Structure" (Trans., 1905, **87**, 1272), deal with camphorquinonephenylhydrazone and put forward two new formulæ. They base their conclusions upon the values of the molecular rotation and also upon the colour of the hydrazone compounds of camphorquinone. They say that the stable form of the phenylhydrazone is colourless and that the phenylmethylhydrazone is faintly yellow, whilst the phenylbenzyl compound is colourless and the diphenylhydrazone is as coloured as camphorquinone itself. For this reason, as well as for the reason of optical rotation, they consider the diphenylhydrazone to have the usually accepted ketonic structure and the other substances to have one of the formulæ:

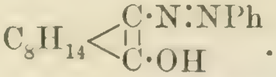


or



where X is either H, CH_3 or C_7H_7. They believe that this conclusion is incontrovertible, and point out that it involves the wandering of the methyl and the benzyl group.

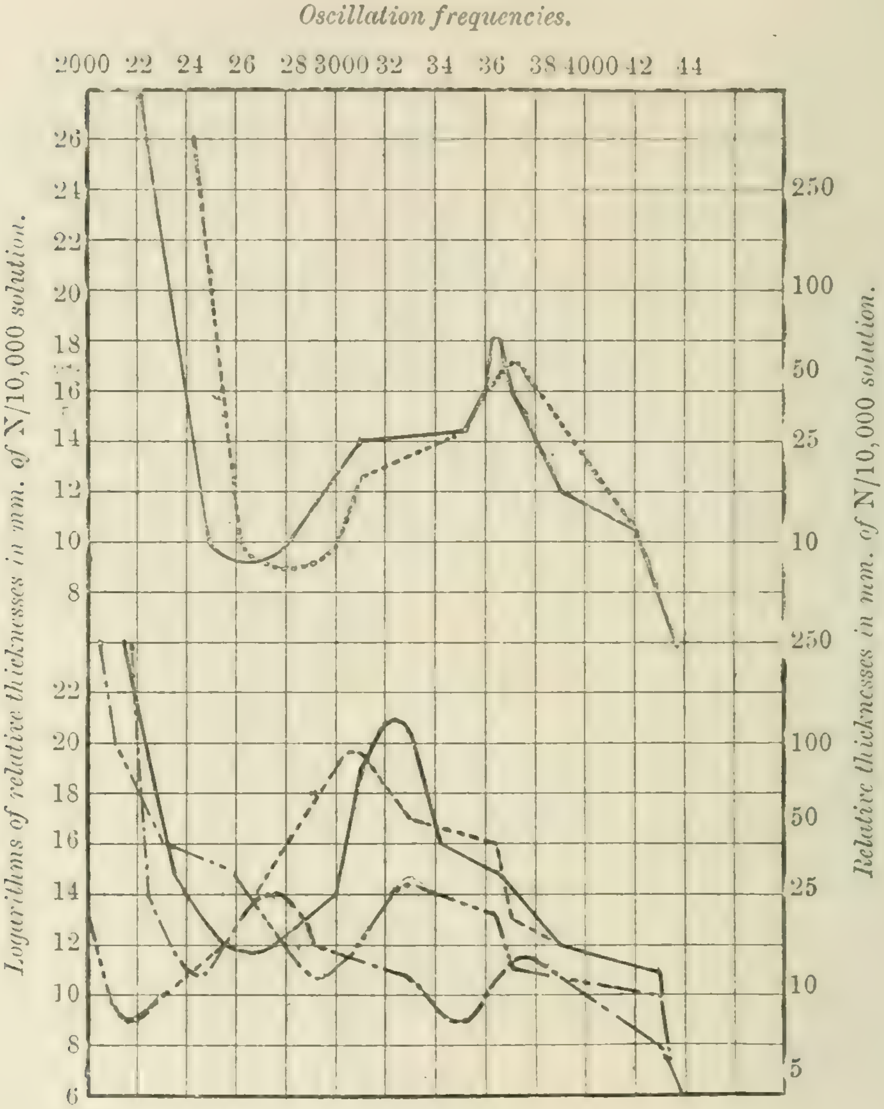
Again, Lapworth and Hann (Trans., 1902, **81**, 1514), in dealing with the mutarotation of camphorquinonephenylhydrazone, for want of definite evidence, appear to accept Betti's conclusion (*Ber.*, 1899, **32**, 1995) that the stable form of this substance has the enolic configuration:



$$C_8H_{14}<\begin{matrix} C\cdot N\colon NPh \\ \| \\ C\cdot OH \end{matrix}\ .$$

The curves showing the absorption exhibited by the various compounds examined are given in Figs. 1—7. In the upper part of Fig. 1 are shown the absorption spectra of glyoxalphenylosazone and glyoxalphenylmethylosazone. It may be pointed out that these curves are typical of the osazones and hydrazones of α-diketones which do not contain a phenyl group. The absorption shows a broad band with head at an oscillation frequency of from 2700 to 2800 and a sudden extension or shallow band on the side of shorter wave-lengths and at slightly greater concentration. As can be seen from the figures, this type of curve is given by the phenylhydrazones of diacetyl, pyruvic aldehyde, and camphorquinone, the osazones of glyoxal, diacetyl, and pyruvic aldehyde, the phenylmethylosazone of glyoxal, the phenylmethyl-, the phenylbenzyl-, the diphenyl- and the *p*-bromophenyl-hydrazones of camphorquinone. In the first place, it can be seen at once on reference to the curves shown in Fig. 3 that almost identical spectra are given by the camphorquinone compounds in neutral solution. This fact is

FIG. 1.

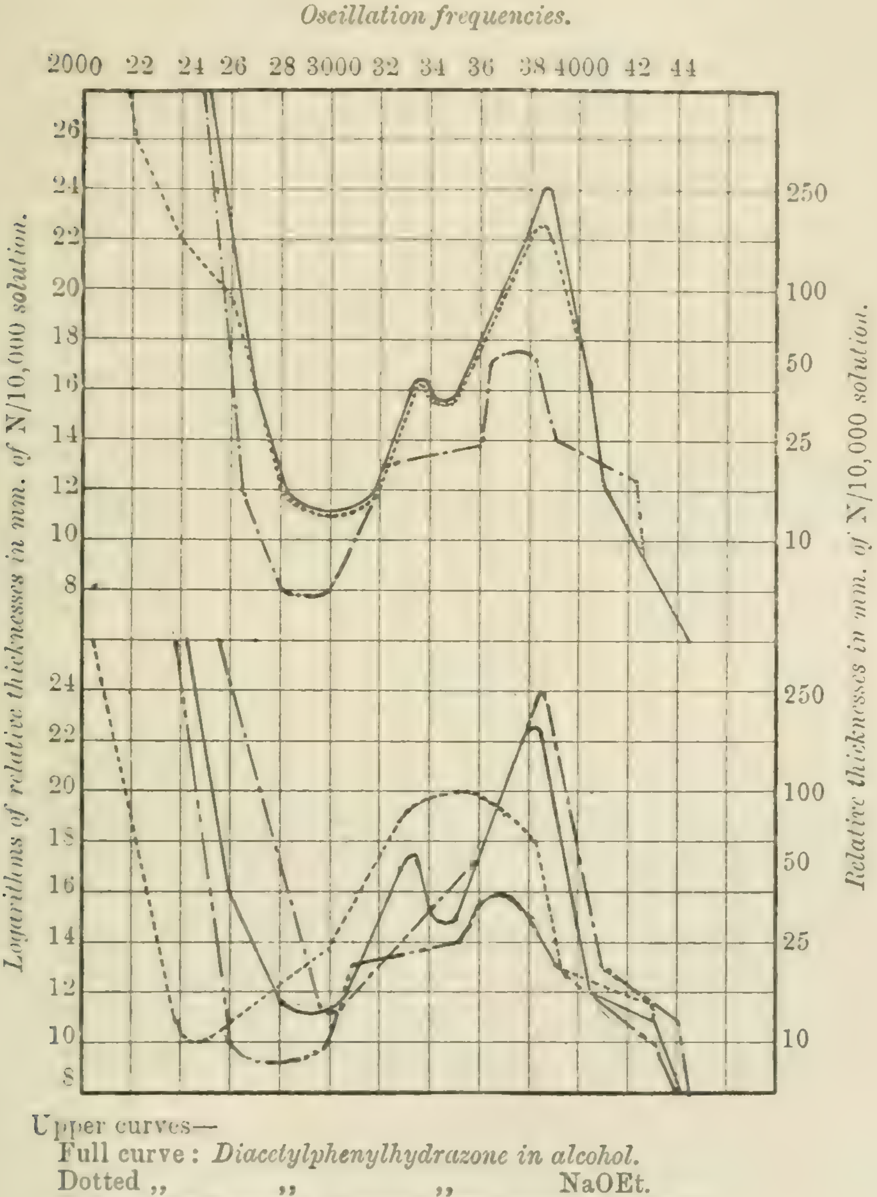


Upper curves—
Full curve: *Glyoxalphenylosazone.*
Dotted ,, *Glyoxalphenylmethylosazone.*

Lower curves—
Full curve: *Phenylglyoxalphenylhydrazone.*
Dotted ,, *Phenylglyoxalphenylhydrazone in* NaOEt.
Dot and dash curve: *Phenylglyoxalosazone.*
Dash and two dots curve: *Phenylglyoxalmethylosazone.*

an undoubted proof that Armstrong and Robertson's contention of the different constitution of the diphenylhydrazone is untenable ; all these substances must have the same constitution.

FIG. 2.



Upper curves—

Full curve : *Diacetylphenylhydrazone in alcohol.*

Dotted ,, ,, ,, NaOEt.

Dot and dash curve : *Diacetylphenylosazone in alcohol.*

Lower curves—

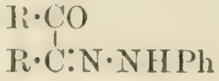
Full curve : *Pyruvic aldehydephenylhydrazone in alcohol.*

Dotted ,, ,, ,, NaOEt.

Dot and dash curve : *Pyruvic aldehydephenylmethylhydrazone.*

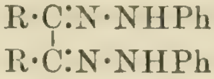
Dash and two dots curve : *Pyruvic aldehydeosazone.*

Inasmuch as the above osazones and hydrazones all exhibit the same type of absorption, the only difference being a slight variation in the relative persistence of the two absorption bands, there can be no doubt that they all possess an analogous constitution which must of necessity be:



$$\begin{array}{l} R\cdot CO \\ \;\;| \\ R\cdot C{:}N\cdot NHPh \end{array}$$

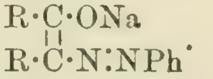
Hydrazone.



$$\begin{array}{l} R\cdot C{:}N\cdot NHPh \\ \;\;| \\ R\cdot C{:}N\cdot NHPh \end{array}$$

Osazone.

When, however, the phenylhydrazones are dissolved in an alcoholic solution of sodium ethoxide, the absorption spectra indicate that their constitution is more or less modified. In the upper portion of Fig. 2 the dotted curve is that obtained with diacetylphenylhydrazone in the presence of excess of sodium ethoxide. The upper portion of the curve is shifted considerably towards the red, indicating the incipient formation of a new absorption band. This band is slightly more marked in the case of camphorquinonephenylhydrazone in alkaline solution, whilst with camphorquinone-*p*-bromophenylhydrazone the new band is well developed. This new absorption band, situated as it is, nearer the red, suggests at once the azo-configuration, inasmuch as the phenylhydrazones of simple aldehydes and ketones tend readily to pass into this form (Baly and Tuck, *loc. cit.*). If the above ketonic structure be accepted for the hydrazones in neutral solution, it may be expected that in the presence of excess of sodium ethoxide they would tend to favour the enolic form:



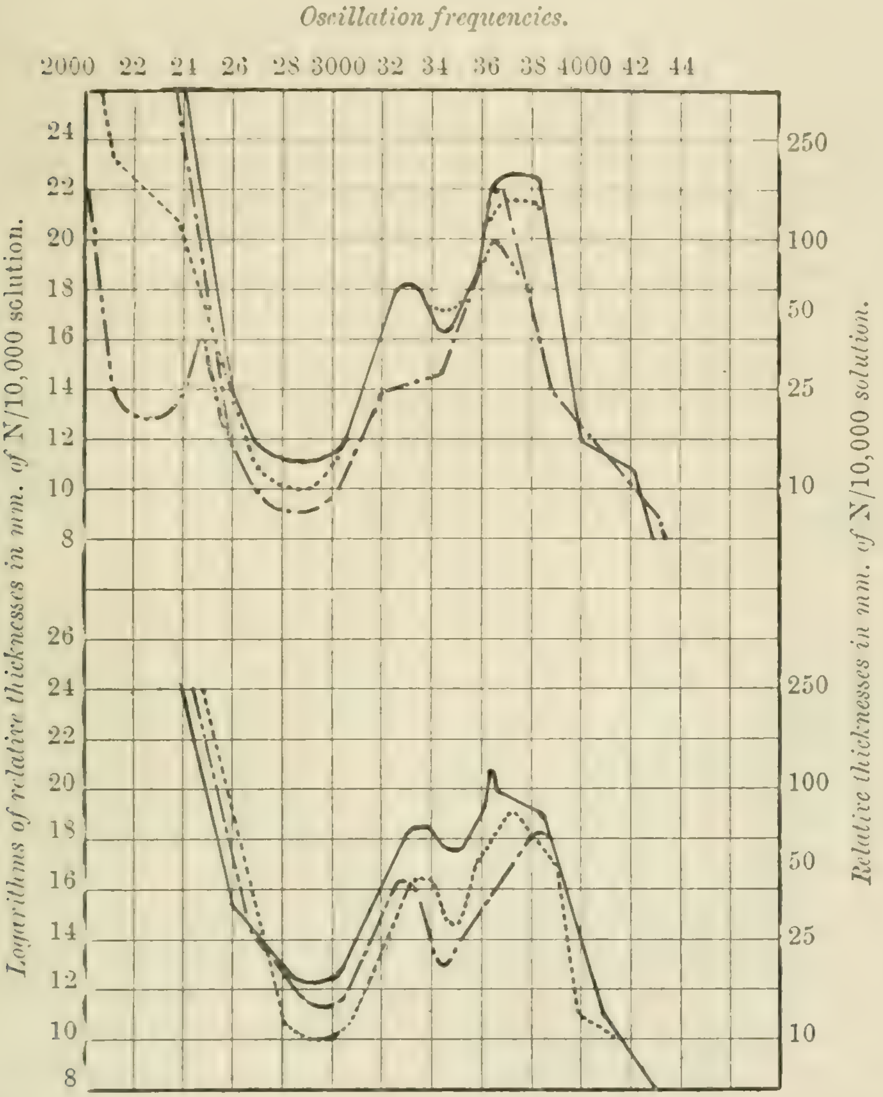
$$\begin{array}{l} R\cdot C\cdot ONa \\ \;\;\| \\ R\cdot C\cdot N{:}NPh\cdot \end{array}$$

This configuration would at once explain the new absorption band, because, as already mentioned, the azo-configuration produces an absorption band in the same region, and, further, the fact that the azo-linking is in this case conjugated with a double linking between carbon atoms would explain the band being at somewhat less concentration than that observed with the azo-form of the simple aldehyde- and ketone-phenylhydrazones. For these two reasons we may safely attribute the new band to the enolic form and say that the presence of excess of alkali tends to favour this form.

We do not in any way mean that the whole of the hydrazone is enolic under these conditions; the amount of the enolic form present may certainly be estimated from the persistence of the new absorption band. Thus it may be said that in the presence of the same amount of alkali much more of camphorquinone-*p*-bromophenylhydrazone is in the enolic form than the phenylhydrazones of diacetyl or camphorquinone. These conclusions are just the opposite of those given by Betti and accepted by Lapworth and Hann, for it is to the stable form of camphorquinonephenylhydrazone that we assign the ketonic configuration. This, however, in no way interferes with Lapworth and Hann's results or detracts from the value of their work.

Although the phenylhydrazone and osazone of pyruvic aldehyde are quite regular, the effect of methylating the former in presence of alkali is somewhat abnormal. On reference to the lower curves in Fig. 2 it will be seen that the dotted curve, representing the absorption of pyruvic aldehydephenylhydrazone in presence of alkali, is distinctly different from those of the other hydrazones in alkaline solution.

FIG. 3.

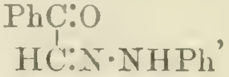


Upper curves—
Full curve : *Camphorquinonephenylhydrazone in alcohol.*
Dotted ,, ,, ,, NaOEt.
Dash and dot curve : *Camphorquinone-*p*-bromophenylhydrazone in alcohol.*
Dash and two dots curve : ,, ,, NaOEt.

Lower curves—
Full curve : *Camphorquinonephenylmethylhydrazone.*
Dotted ,, *Camphorquinonephenylbenzylhydrazone.*
Dash and dot curve : *Camphorquinonediphenylhydrazone.*

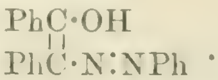
Further, the absorption of the phenylmethylhydrazone (obtained by methylation) as shown by the dot and dash curve is also different from the normal type. It is difficult to account for these two abnormal curves. Japp and Klingemann's (Trans., 1888, **53**, 519) results seem to prove conclusively that during methylation the methyl group attaches itself to the nitrogen atom in the normal manner, but the somewhat abnormal behaviour in presence of alkali and the different absorption shown by the resulting methyl derivative would appear to oppose this.

We have also examined the compounds of phenylhydrazine with phenylglyoxal and with benzil, but in these cases the results are somewhat complicated by the presence of the phenyl group. The absorption of the phenylhydrazone of phenylglyoxal in neutral and alkaline solution is shown by the lower full and dotted curves respectively in Fig. 1. The former shows a single broad band at the oscillation frequency 2670, whilst in the latter the absorption band is shifted considerably towards the red and has its head at the frequency 2180. This is analogous to the phenylhydrazones of diacetyl, &c., but the shape of the curves is modified, as would be expected by the presence of the phenyl group of the parent substance. In the compound:



$$\begin{array}{l}\mathrm{PhC{:}O}\\ \quad\;|\\ \mathrm{HC{:}N{\cdot}NHPh},\end{array}$$

the isorropesis between the two conjugated double linkings will necessarily be interfered with by the adjacent phenyl group, for it has been shown that the grouping Ph·CO·, as in acetophenone (Baly and Collie, Trans., 1905, **87**, 1331), forms a system with a definite vibration period of its own. Thus it is evident that the carbonyl group is not free entirely to exert its influence on the adjacent C:N linking. It is to be expected, therefore, that the curve of absorption of this compound would be modified. The same argument exactly applies to the case of the phenylhydrazone of benzil, the absorption of which in neutral and alkaline solution is shown by the full and dotted curves respectively in Fig. 4. In this compound there are two phenyl groups conjugated with the hydrazone double linking, and the effect of this is especially noticeable in the benzilphenylhydrazone in alkaline solution. This curve shows a very broad absorption band such as would be caused by the conjugation of the two phenyl groups with the double linkings as expressed by the formula:



$$\begin{array}{l}\mathrm{PhC{\cdot}OH}\\ \quad\;||\\ \mathrm{PhC{\cdot}N{:}NPh}\;.\end{array}$$

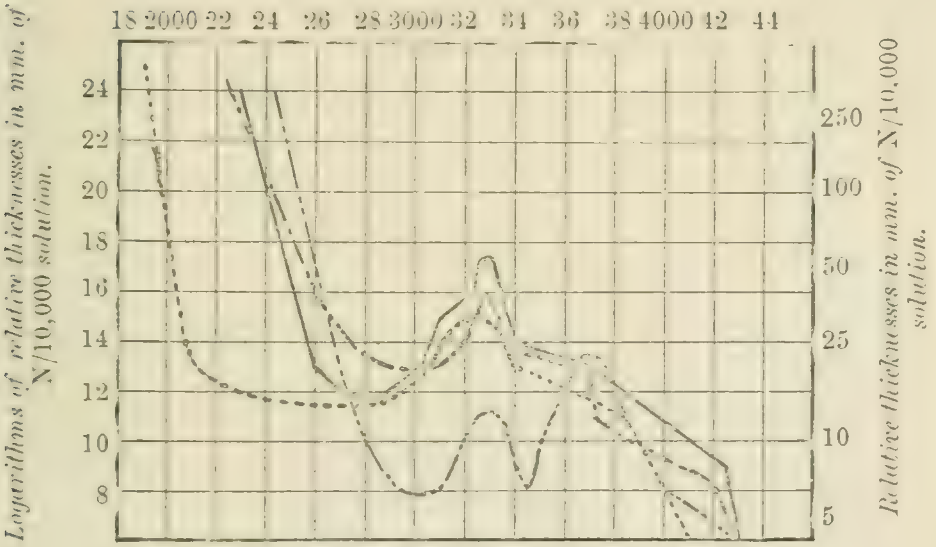
The absorption of benzilphenylmethylhydrazone is shown by the dot and dash curve in Fig. 4. As would be expected, it is similar to that of the phenylhydrazone in neutral solution.

We have also examined the absorption spectra of the benzilosazones.

We are indebted to Dr. Chattaway for three specimens of these compounds, one of the α-compound prepared from benzil itself, one of the α-compound prepared from the β-modification and one of the β-compound. All three gave identically the same absorption as shown by the dash and two dots curve in Fig. 4. This conforms to the normal type, the only difference being that the second band at frequency 3430 is rather more accentuated. The identical absorption shown by these three osazones is very striking and is a clear proof that they have the same configuration in solution. As the absorption is normal, these substances must have the formula :

$$\begin{array}{l}\mathrm{PhC{:}N{\cdot}NHPh}\\ \;\;|\\ \mathrm{PhC{:}N{\cdot}NHPh}\end{array}.$$

FIG. 4.

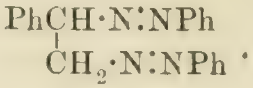


Full curve : *Benzilphenylhydrazone in alcohol.*
Dotted ,, ,, ,, ,, ,, *with* NaOEt.
Dot and dash curve : *Benzilphenylmethylhydrazone.*
Dash and two dots curve : *Benzilosazones.*

The absorption of the osazone and methylosazone of phenylglyoxal is shown by the dot and dash and the dash and two dots curves in Fig. 1. The latter is very similar to that of benzil, the only difference being that the second band at 3430 is very shallow; this undoubtedly shows that the compound has the normal constitution :

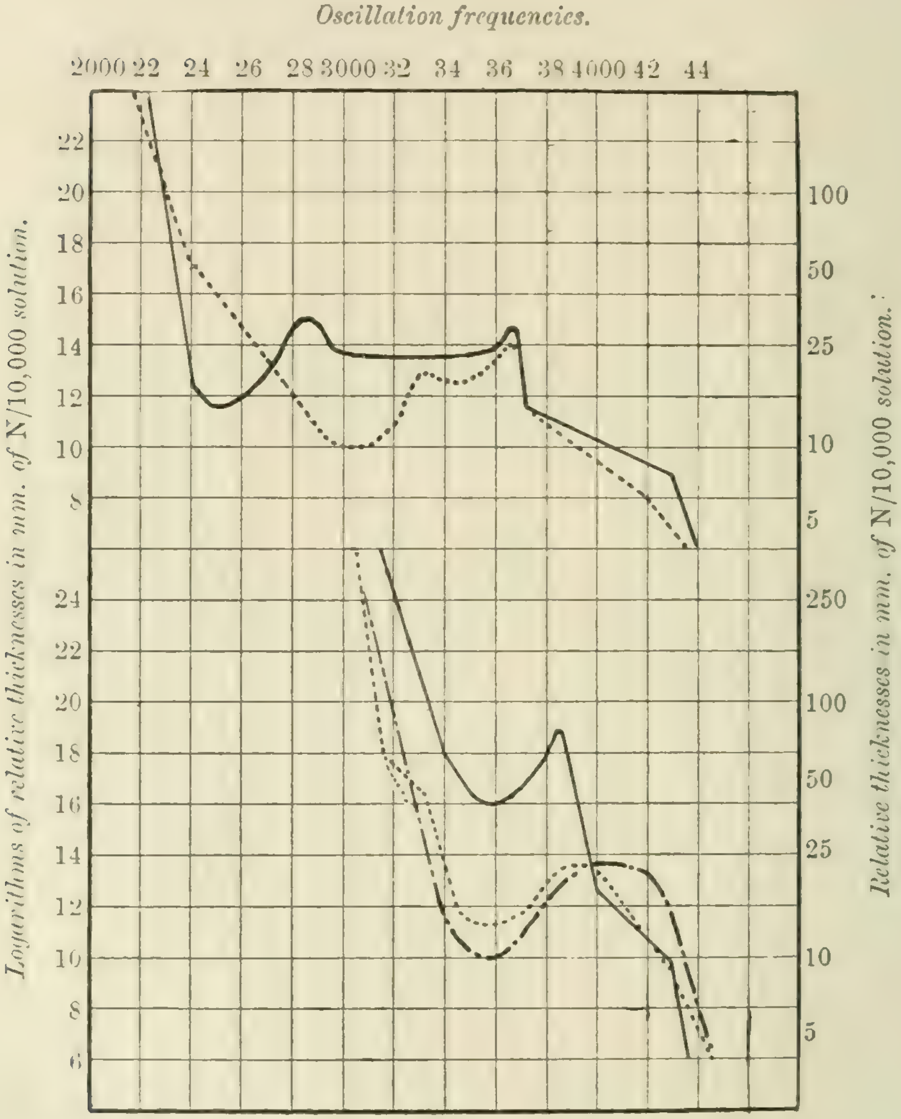
$$\begin{array}{l}\mathrm{PhC{:}N{\cdot}NMePh}\\ \;\;|\\ \mathrm{HC{:}N{\cdot}NMePh}\end{array}.$$

The osazone, however, is quite different and shows its principal absorption band at a frequency of 2430. This at once suggests the azo-configuration, and we therefore believe that this substance is partly or entirely in the azo-form, thus:



$$\begin{array}{l}\mathrm{PhCH{\cdot}N{:}NPh}\\ \quad|\\ \quad\mathrm{CH_2{\cdot}N{:}NPh}\end{array}$$

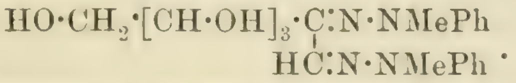
FIG. 5.



Upper curves—
Full curve: *Glucosazone.*
Dotted ,, *Glucosemethylosazone.*

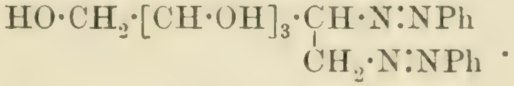
Lower curves—
Full curve: *Glucosephenylhydrazone* (*a*).
Dotted ,, ,, ,, ,, ,, *after standing in the dark.*
Dot and dash curve: *Glucosephenylmethylhydrazone.*

We have further examined the osazone and the methylosazone of glucose, the absorption of which is shown by the upper full and dotted curves in Fig. 5. The latter is again quite normal, and therefore indicates the normal configuration:



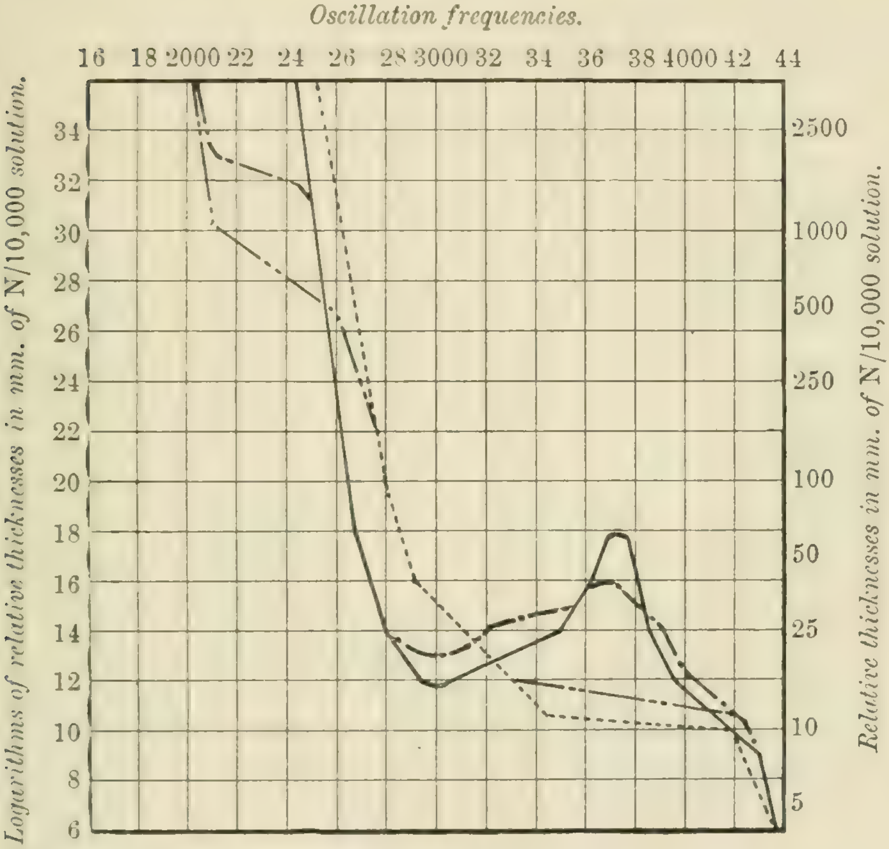
$$\begin{array}{l} HO\cdot CH_2\cdot[CH\cdot OH]_3\cdot \underset{|}{C}:N\cdot NMePh \\ \qquad\qquad\qquad\qquad\quad HC:N\cdot NMePh\ \cdot \end{array}$$

The osazone, however, like phenylglyoxalosazone, is quite abnormal, showing an azo-band, and we therefore are of the opinion that this substance also is partly or entirely in the azo-form:



$$\begin{array}{l} HO\cdot CH_2\cdot[CH\cdot OH]_3\cdot \underset{|}{C}H\cdot N:NPh \\ \qquad\qquad\qquad\qquad\quad CH_2\cdot N:NPh\ \cdot \end{array}$$

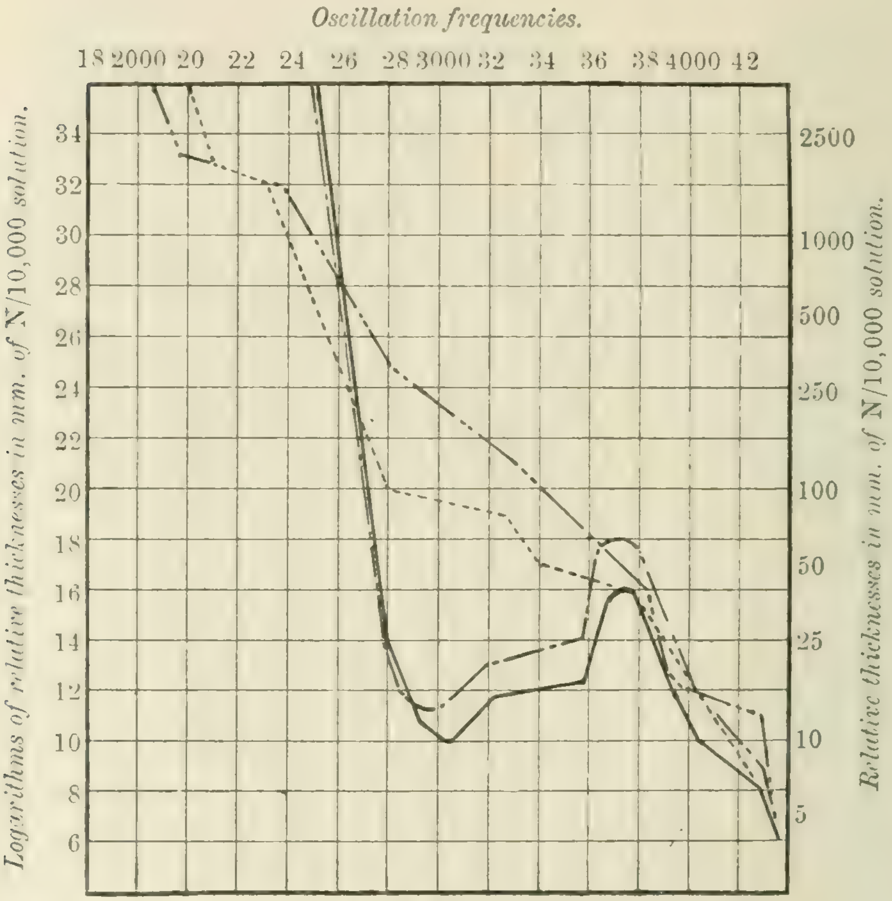
FIG. 6.



Full curve: *Benzoinphenylhydrazone* (α).
Dotted ,, ,, ,, ,, (β).
Dot and dash curve: *Benzoinphenylhydrazone* (α) *after exposure to light.*
Dash and two dots curve: ,, ,, ,, (β) ,, ,, ,,

An interesting point arises in the case of glucosazone, namely, why the introduction of the phenylhydrazine residue into glucose renders the adjacent hydroxyl group readily oxidisable by a further molecule of phenylhydrazine, and why, when the osazone has been formed, the adjacent hydroxyl group is not oxidisable. In order to investigate this point we have examined the absorption spectra of the phenylhydrazones of two α-hydroxyketones and of glucose itself. This was undertaken with the view of determining whether the hydroxyl group adjacent to the C:N linking has any influence. The absorption of the phenylhydrazones and the phenylmethylhydrazone of glucose is shown by the full, dotted, and dot and dash curves in the lower half of Fig. 5. The three curves are of the same type, but that of the α-hydrazone shows its band at a greater concentration. This solution, on standing in the dark (with formation of the β-modification), gives a curve closely approximating to that of the phenylmethylhydrazone. As the change is probably due to the glucose residue, it may be assumed that the two hydrazones are quite normal and have the same constitution as the phenylmethylhydrazone. The curve is very similar to that of propaldehydephenylhydrazone.

FIG. 7.



Full curve : *Deoxybenzoinphenylhydrazone.*
Dotted ,, ,, ,, ,, ,, *after exposure to light.*
Dot and dash curve : *Benzoylcarbinolphenylhydrazone.*
Dash and two dots curve ,, ,, ,, ,, *after exposure to light.*

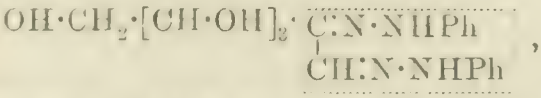
In Fig. 7 the dot and dash curve represents the absorption of benzoylcarbinolphenylhydrazone, and this differs slightly from that of acetophenonephenylhydrazone. The persistence of the former is somewhat less, and also there is a sudden extension from 3200 to 3600. The presence of the adjacent hydroxyl group therefore produces a small effect.

The absorption spectra of the phenylhydrazones of propaldehyde and acetophenone were described in the previous paper (Baly and Tuck, *loc. cit.*). Comparison may also be made between the absorption of the phenylhydrazones of benzoin and deoxybenzoin. The curve of the *a*-phenylhydrazone of benzoin is shown in Fig. 6 (full curve) and of deoxybenzoinphenylhydrazone in Fig. 7 (full curve), and again a small difference in the shape of the curves is noticeable.

In Fig. 6 the dotted curve is that of the so-called benzoin-β-phenylhydrazone; this absorption is quite abnormal and shows that this substance cannot be a true hydrazone. We have thus a slight but undoubted evidence that the adjacent hydroxyl group has some influence. The most striking effect, however, is to be noticed when the change of the *a*-hydroxyketonephenylhydrazones to the azo-form is observed. As recorded in the previous paper, all the phenylhydrazones of ketones change very rapidly to the azo-form under the influence of light, the alteration taking place completely in from 0·5 to 3 hours. This change to the azo-form in the case of the hydroxyketonephenylhydrazones takes place very slowly and requires as long as from two to three days. The change of the hydrazone to the azo-form is no doubt due to the tendency of the double linking to approach the phenyl group, and the fact that the hydroxyl group retards this change is an undoubted proof of some mutual influence between the hydroxyl group and the C:N linking of the hydrazone. It is the mutual influence and its effect on the hydroxyl group which renders the latter so easily oxidisable by phenylhydrazine with the resulting formation of the osazone.

Moreover, it is evident that any agent which tends to retard the change to the azo-form would also tend to accelerate the formation of the osazone from a hydroxyketonephenylhydrazone. In the previous paper it was shown that acetic acid materially retards the change of a hydrazone to the azo-form; consequently acetic acid should act as a catalytic agent in the formation of osazones, a fact which is well known.

When an osazone such as glucosazone has once been formed, the influence of the double linking on the next hydroxyl group is negligible *owing to the fact that the two adjacent double linkings are conjugated together.* In glucosazone



$$\begin{array}{l} \mathrm{OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}}\boxed{\begin{array}{l}\mathrm{C{:}N{\cdot}NHPh}\\ \mathrm{|}\\ \mathrm{CH{:}N{\cdot}NHPh}\end{array}} \end{array},$$

the linkings within the dotted square form a condensed system which is complete in itself, so that the C:N linking next the hydroxyl is, so to speak, entirely occupied and has no free affinity to act on the adjacent hydroxyl. For this reason the hydroxyl group is not abnormal and so is not oxidisable by phenylhydrazine.

Conclusions.

1. The phenylhydrazones and osazones of the α-diketones exist in the ketonic form in neutral solution; phenylglyoxalosazone and glucosazone, however, appear to be partly or entirely in the azo-form.

2. In alkaline solution, the phenylhydrazones tend to favour the enolic configuration.

3. In the phenylhydrazones of the α-hydroxyketones, the effect of the adjacent hydroxyl is very marked; it retards very considerably the change of the hydrazone to the azo-compound. This mutual influence of the hydroxyl group and the C:N linking no doubt renders the former readily oxidisable.

4. In the osazones of the carbohydrates, the two C:N linkings are conjugated and so form a condensed system with little or no affinity to act on the adjacent hydroxyl. For this reason, the hydroxyl group is normal and not oxidisable by phenylhydrazine.

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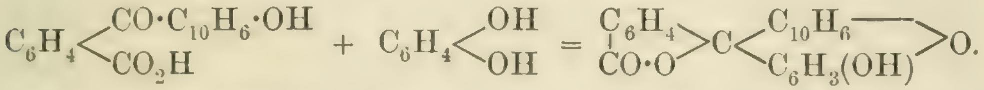
CL.—*The Fluoresceins and Eosins from 4-Hydroxyphthalic, 4-Methoxyphthalic, and Hemipinic Acids.*

By ARTHUR FRIEDL, CHARLES WEIZMANN, and MAX WYLER.

HYDROXYFLUORESCEIN was first prepared by Baeyer (*Ber.*, 1877, **10**, 1079) from 4-hydroxyphthalic acid and was found to exhibit very little fluorescence; the corresponding eosin was also prepared and was found to dye silk in redder shades than are produced by ordinary eosin. As we were interested in the comparative study of the coloured derivatives of 4-hydroxy- and 4-methoxy-phthalic acids in relation to those of phthalic acid, we prepared the fluoresceins and eosins from these acids. Our chief aim was to discover how the fluorescence of hydroxyfluorescein and hydroxyeosin was affected by converting the hydroxyl into a methoxyl group, and being induced by our results to investigate the effect produced by the introduction of a further methoxyl group, we prepared the corresponding derivatives from hemipinic acid. It was found that, both in the fluoresceins and the eosins, the alkaline solutions of the hydroxy-derivatives possessed very little fluorescence, whilst the methoxy-derivatives exhibited an exceedingly strong fluorescence. On the other hand, the dimethoxy-derivatives were found to be very little more fluorescent than the hydroxy-derivatives.

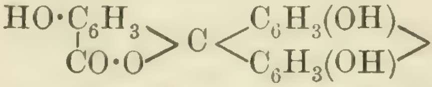
Another point on the subject of the fluoresceins which we were desirous of investigating was the substitution of one of the resorcinol groups in ordinary fluorescein by a monohydroxy-compound. It was found possible to obtain such a substituted fluorescein by condensing hydroxynaphthoylbenzoic acid with resorcinol :



$$C_6H_4{<}\begin{matrix}CO\cdot C_{10}H_6\cdot OH\\ CO_2H\end{matrix} + C_6H_4{<}\begin{matrix}OH\\ OH\end{matrix} = \begin{matrix}C_6H_4\\ |\\ CO\cdot O\end{matrix}{>}C{<}\begin{matrix}C_{10}H_6\text{——}\\ C_6H_3(OH)\end{matrix}{>}O.$$

The resulting *a-naphtholresorcinolphthalein anhydride* in some of its properties, and especially in its fluorescence, showed a strong resemblance to hydroxyfluorescein. It would thus appear that the introduction of a hydroxy-group in the phthalic acid nucleus of fluorescein has nearly the same effect as the elimination of one hydroxy-group from fluorescein itself.

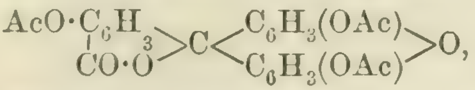
EXPERIMENTAL.

Hydroxyfluorescein,  $\begin{matrix}HO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}{>}O.$ — This substance is prepared by adding a mixture of 4-hydroxyphthalic anhydride (16·5 grams) and resorcinol (22 grams) to a solution of zinc chloride (60 grams) in water (40 c.c.) and heating the mixture to 140—150° for five hours. The product is poured into water, the precipitate extracted three times with boiling water, then dissolved in very dilute sodium hydroxide, and reprecipitated with hydrochloric acid. It separates from dilute methyl alcohol as a red powder melting at about 350° :

0·1130 gave 0·2854 CO_2 and 0·0386 H_2O. C = 68·87 ; H = 3·79.

$C_{20}H_{12}O_6$ requires C = 68·96 ; H = 3·42 per cent.

Hydroxyfluorescein dissolves in alkalis producing slightly fluorescent, orange-yellow solutions, and in concentrated sulphuric acid giving a canary-yellow, fluorescent solution. It is slightly soluble in hot water, and more soluble in dilute than in glacial acetic acid. When boiled with acetic anhydride, it dissolves to a yellow solution, which when poured into water yields *hydroxyfluorescein triacetate,*



$$\begin{matrix}AcO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OAc)\\ C_6H_3(OAc)\end{matrix}{>}O,$$

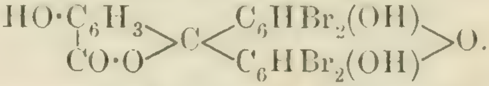
as a resinous solid which crystallises from acetic acid in pale yellow needles melting at 196—198° :

0·1220 gave 0·2936 CO_2 and 0·0459 H_2O. C = 65·63 ; H = 4·18.

$C_{26}H_{18}O_9$ requires C = 65·82 ; H = 3·79 per cent.

Hydroxyfluorescein triacetate dissolves in sulphuric acid producing a yellow, fluorescent solution. It is not readily attacked by cold potassium hydroxide, but is quickly hydrolysed by the hot alkali.

Tetrabromohydroxyfluorescein [*Hydroxyeosin*],



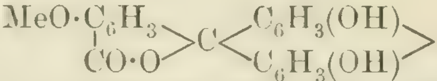
$$\begin{matrix}HO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6HBr_2(OH)\\ C_6HBr_2(OH)\end{matrix}>O.$$

—This compound separates when a solution of hydroxyfluorescein (7 grams) in glacial acetic acid is heated with bromine (13 grams) for two hours in a reflux apparatus. The product is poured into water, and the precipitate crystallised from nitrobenzene:

0·2405 gave 0·2751 AgBr. Br = 48·67.

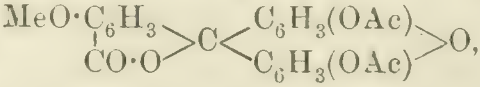
$C_{20}H_8O_6Br_4$ requires Br = 48·19 per cent.

Hydroxyeosin forms an orange-coloured powder melting indefinitely at 200°. Its alkaline solutions are red, exhibiting very little fluorescence. It dyes chrome-mordanted wool a bluer shade than does ordinary eosin.

Methoxyfluorescein,  $\begin{matrix}MeO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}>O$.—This derivative is prepared from 4-methoxyphthalic anhydride by the same method as that given for hydroxyfluorescein:

0·1188 gave 0·3012 CO_2 and 0·0432 H_2O. C = 69·14; H = 4·04.

$C_{21}H_{14}O_6$ requires C = 69·61; H = 3·86 per cent.

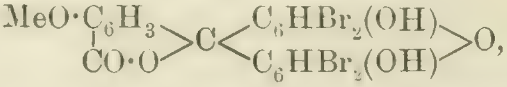
Methoxyfluorescein forms a red powder melting at about 300°. It dissolves in alkalis, giving yellow solutions which exhibit intense fluorescence; its solutions in acetic acid, alcohol, and sulphuric acid are pale yellow and only slightly fluorescent. When boiled with acetic anhydride, it dissolves to a yellow solution, forming *methoxyfluorescein diacetate*,  $\begin{matrix}MeO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6H_3(OAc)\\ C_6H_3(OAc)\end{matrix}>O$, which crystallises from acetic acid in white needles melting at 118—120°:

0·1150 gave 0·2835 CO_2 and 0·0458 H_2O. C = 67·23; H = 4·42.

$C_{25}H_{18}O_8$ requires C = 67·26; H = 4·03 per cent.

Methoxyfluorescein diacetate dissolves in sulphuric acid, forming a yellow, fluorescent solution. It is readily hydrolysed by hot potassium hydroxide, but scarcely affected by the cold alkali.

Tetrabromomethoxyfluorescein [*Methoxyeosin*],



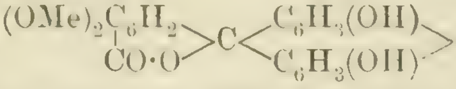
$$\begin{matrix}MeO\cdot C_6H_3\\ |\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6HBr_2(OH)\\ C_6HBr_2(OH)\end{matrix}>O,$$

is produced by the bromination of methoxyfluorescein in acetic acid solution:

0·2648 gave 0·2990 AgBr. Br = 48·04.

$C_{21}H_{10}O_6Br_4$ requires Br = 47·49 per cent.

Methoxyeosin forms an orange-red-coloured powder melting indefinitely above 200°. It forms a yellow solution with concentrated sulphuric acid, and its alkaline solutions are red and strongly fluorescent. It dyes chrome-mordanted wool a yellower shade than does eosin.

Dimethoxyfluorescein, 

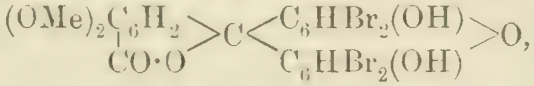
$\begin{matrix}(OMe)_2C_6H_2\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}>O$

—This substance is obtained when hemipinic anhydride is substituted for hydroxyphthalic anhydride in the process given for the preparation of hydroxyfluorescein:

0·1216 gave 0·2988 CO_2 and 0·0478 H_2O. C = 67·00; H = 4·36.
$C_{22}H_{16}O_7$ requires C = 67·34; H = 4·08 per cent.

Dimethoxyfluorescein forms a yellowish-brown powder melting indefinitely at 280°. It is soluble in alkalis, yielding yellowish-brown solutions only moderately fluorescent. When heated with acetic anhydride, it yields a yellow *acetyl* derivative melting indefinitely at 110°.

Tetrabromodimethoxyfluorescein [*Dimethoxyeosin*],



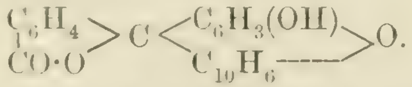
$\begin{matrix}(OMe)_2C_6H_2\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6HBr_2(OH)\\ C_6HBr_2(OH)\end{matrix}>O,$

is obtained by brominating dimethoxyfluorescein in acetic acid solution:

0·2305 gave 0·2531 AgBr. Br = 46·63.
$C_{22}H_{12}O_7Br_4$ requires Br = 45·19 per cent.

Dimethoxyeosin forms a red powder decomposing at 250°. With alkalis it gives a deep red solution which is very slightly fluorescent, and its solution in sulphuric acid is yellow. It dyes chrome-mordanted wool a yellower shade than does eosin.

a-Naphtholresorcinolphthalein Anhydride,

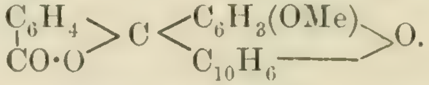


$\begin{matrix}C_6H_4\\ CO\cdot O\end{matrix}>C<\begin{matrix}C_6H_3(OH)\\ C_{10}H_6\text{——}\end{matrix}>O.$

—This compound is prepared by heating a mixture of 1-hydroxynaphthoylbenzoic acid (15 grams), resorcinol (5·5 grams), and concentrated sulphuric acid (80 grams) on the water-bath for an hour. The red solution is poured into water, the precipitate collected, washed with water, and purified by dissolving in a large quantity of very dilute sodium hydroxide, and reprecipitating with hydrochloric acid. It is a yellowish-red powder, which is very difficult to obtain pure by recrystallisation from ordinary organic solvents. It dissolves in alkalis to yellowish-brown, fluorescent solutions; in alcohol or acetic acid it yields pale orange, and in sulphuric acid orange-red, fluorescent solutions.

When dissolved in sodium hydroxide and shaken with dimethyl sulphate, a brick-red precipitate appears, which is the

Methyl Ether of a-Naphtholresorcinolphthalein Anhydride,



$$\begin{array}{l}C_6H_4\\ |\\ CO\cdot O\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_3(OMe)\\ C_{10}H_6\text{———}\end{array}\!\!>O.$$

—This crystallises from dilute acetic acid or methyl alcohol in leaflets melting at about 220°:

0·1233 gave 0·3546 CO_2 and 0·0460 H_2O. C = 78·48; H = 4·14.

$C_{25}H_{16}O_4$ requires C = 78·95; H = 4·21 per cent.

This substance dissolves in concentrated sulphuric acid giving an orange, fluorescent solution.

The *acetyl* derivative of *a*-naphtholresorcinolphthalein anhydride is prepared by boiling this compound with acetic anhydride and sodium acetate. It crystallises from alcohol in leaflets melting at 207°:

0·1148 gave 0·3212 CO_2 and 0·0431 H_2O. C = 76·30; H = 4·17.

$C_{26}H_{16}O_5$ requires C = 76·47; H = 3·92 per cent.

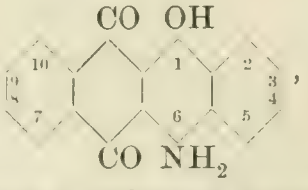
This acetyl compound is hydrolysed slowly by aqueous potassium hydroxide, but readily by cold alcoholic potash.

MANCHESTER UNIVERSITY.

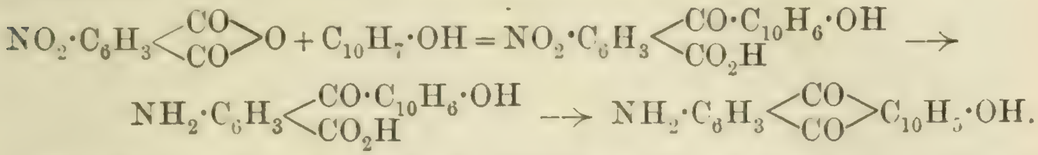
CLI.—*Derivatives of Naphthacenequinone. Part II.*

By WILLIAM HENRY BENTLEY, ARTHUR FRIEDL, and CHARLES WEIZMANN.

IN a former paper (this vol., p. 417), we described an aminohydroxynaphthacenequinone containing both substituent groups in the naphthalene ring:



and having observed a marked difference between hydroxy-derivatives of 1-hydroxynaphthacenequinone substituted in the benzene and in the naphthalene rings, it appeared to be of interest to make the same comparison with the amino-derivatives of 1-hydroxynaphthacenequinone. In order to prepare aminohydroxynaphthacenequinones containing the amino-group in the benzene ring, we condensed the two nitrophthalic acids with *a*-naphthol by means of boric acid, reduced the resulting nitro-*a*-hydroxynaphthoylbenzoic acid to the amino-acid, and condensed this to the aminohydroxynaphthacenequinone by warming with concentrated sulphuric acid :



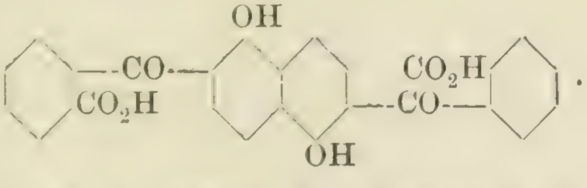
$$NO_2\cdot C_6H_3 < \substack{CO\\CO} > O + C_{10}H_7\cdot OH = NO_2\cdot C_6H_3 < \substack{CO\cdot C_{10}H_6\cdot OH\\CO_2H} \longrightarrow$$

$$NH_2\cdot C_6H_3 < \substack{CO\cdot C_{10}H_6\cdot OH\\CO_2H} \longrightarrow NH_2\cdot C_6H_3 < \substack{CO\\CO} > C_{10}H_5\cdot OH.$$

Unfortunately, these reactions proceeded with very bad yields, and the aminohydroxynaphthacenequinones obtained were in such small quantity that no detailed investigation of their properties was possible. We were able to observe, however, that considerable difference exists between the aminohydroxynaphthacenequinones having the amino-group in the benzene and in the naphthalene rings. Thus, when the amino-group is contained in the benzene ring, the solution of the compound in concentrated sulphuric acid is very much bluer than that of the corresponding compound containing the amino-group in the naphthalene ring, and, further, the solution of the former compound in alcoholic potash is much yellower than that of the latter.

With the object of preparing a naphthacenequinone containing, like alizarin, two hydroxy-groups in the adjacent α- and β-positions, we condensed hemipinic acid with α-naphthol, thus obtaining hydroxydimethoxynaphthoylbenzoic acid, $(OMe)_2C_6H_2(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$, but on treating this acid with concentrated sulphuric acid only a small yield of the condensation product resulted, and this on analysis gave numbers agreeing with a trihydroxymonomethoxynaphthacenequinone, indicating that partial hydrolysis and oxidation had occurred in the condensation.

In our former communication (*loc. cit.*), the condensation product of phthalic acid and 1 : 5-dihydroxynaphthalene was described. As 1 : 5-dihydroxynaphthalene has two hydroxyl groups in the α-position, we condensed two molecular proportions of phthalic acid with one of 1 : 5-dihydroxynaphthalene and succeeded in obtaining 2 : 6-dicarboxybenzoyl-1 : 5-dihydroxynaphthalene :



On treating this acid, however, with fuming sulphuric acid, the corresponding diquinone was not obtained, but a substance giving analytical numbers agreeing with trihydroxynaphthacenequinone together with a sulphonic acid, probably derived from the same substance. In this case, the quinone ring has been closed only on one side, whilst, presumably, on the other side of the naphthalene nucleus the benzoyl has been replaced by a hydroxyl group.

As the condensation of phthalic acid and 1 : 5-dihydroxynaphthalene yielded chiefly the monobenzoyl acid, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_5(OH)_2$, we were in possession of a considerable quantity of this material, and therefore endeavoured to condense it to the quinone without sulphonation taking place, as had occurred in our former experiments (*loc. cit.*). This was found possible to some extent at least, the product being a mixture of the quinone and its sulphonic acid, from which the 1 : 5-dihydroxynaphthacenequinone was easily separated.

EXPERIMENTAL.

3(6)-*Nitro*-1′-*hydroxy*-2-β-*naphthoylbenzoic Acid*,
$NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$.
—3-Nitrophthalic anhydride (50 grams) and boric acid (150 grams) are intimately mixed and heated to partial fusion. The cold mass is then powdered, mixed with α-naphthol (40 grams) and boric acid (75 grams), and heated to 180° for three hours. The product is extracted with boiling water to remove boric acid, and afterwards with dilute aqueous sodium hydroxide; the alkaline solution on acidification yields a resinous precipitate, which is collected and boiled with water and calcium carbonate for several hours. The liquid is filtered cold, and the filtrate on being acidified with hydrochloric acid yields a yellow precipitate which on crystallisation from dilute alcohol separates in orange prisms melting indefinitely at 200°:

0·2034 gave 7·6 c.c. nitrogen at 18° and 756 mm. N = 4·29.

$C_{18}H_{11}O_6N$ requires N = 4·15 per cent.

When the acid is heated with concentrated sulphuric acid or treated in the cold with fuming sulphuric acid, it yields a small quantity of a naphthacenequinone derivative which dissolves in alcoholic potash with a cherry-red, and in sulphuric acid with a violet, colour.

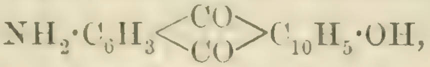
3(6)-*Amino*-1′-*hydroxy*-2-β-*naphthoylbenzoic Acid*,
$NH_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$.
—This acid is obtained by treating the sodium salt of the nitro-acid just described with an excess of ferrous sulphate and sodium carbonate. The mixture is filtered hot and the filtrate acidified with acetic acid; the resulting brown precipitate is dissolved in sodium carbonate and precipitated with sulphurous acid, being obtained as a grey powder melting at 167—170°:

0·1898 gave 7·2 c.c. nitrogen at 17° and 760 mm. N = 4·40.

$C_{18}H_{13}O_4N$ requires N = 4·56 per cent.

The alcoholic solution of this amino-acid gives a dark green coloration with ferric chloride.

When dissolved in concentrated sulphuric acid, it yields a red solution which, when treated with boric acid and fuming sulphuric acid, changes to an intense violet solution. On pouring this into water, the corresponding 7(10)-*amino-1-naphthacenequinone*,



$$NH_2\cdot C_6H_3<\substack{CO\\CO}>C_{10}H_5\cdot OH,$$

is precipitated, which, after filtration, washing with water and dilute ammonia, and drying on porous porcelain, is obtained as a black powder. The yield is extremely small, and in consequence no analytical data can be furnished.

The substance dissolves in concentrated sulphuric acid, yielding an intensely violet solution, which is much bluer than that given by 6-amino-1-hydroxynaphthacenequinone. Its cherry-red solution in alcoholic potash is much yellower than that of 6-amino-1-hydroxynaphthacenequinone.

4(5)-*Nitro-1′-hydroxy-2-β-naphthoylbenzoic Acid.*—This acid is prepared from 4-nitrophthalic acid in a similar manner to that just described from 3-nitrophthalic acid. It forms a yellow powder melting indefinitely at 130—140°:

0·2383 gave 8 c.c. nitrogen at 18° and 756 mm. N = 3·85.

$C_{18}H_{11}O_6N$ requires N = 4·15 per cent.

This nitro-acid is readily soluble in alcohol or acetic acid, but it is difficult to crystallise. With sulphuric acid, it behaves exactly like 3(6)-nitro-1′-hydroxy-2-β-naphthoylbenzoic acid. It is easily reduced with ferrous sulphate and sodium carbonate to

4(5)-*Amino-1′-hydroxy-2-β-naphthoylbenzoic Acid*,

$$NH_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH,$$

which, after isolation and purification like the foregoing amino-acid, is obtained as a yellow powder melting at 160—163°:

0·2446 gave 9·8 c.c. nitrogen at 17° and 760 mm. N = 4·65.

$C_{18}H_{13}O_4N$ requires N = 4·56 per cent.

The alcoholic solution of this acid gives a dark green coloration with ferric chloride.

When treated with fuming sulphuric acid in presence of boric acid, it behaves just like the 3(6)-amino-1′-hydroxy-2-β-naphthoylbenzoic acid, yielding a very small quantity of 8(9)-amino-1-hydroxynaphthacenequinone, which is a dark powder possessing properties exactly similar to those of 7(10)-amino-1-hydroxynaphthacenequinone.

Hydroxydimethoxynaphthoylbenzoic Acid,

$$(MeO)_2C_6H_2(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH.$$

—For the preparation of this acid, hemipinic anhydride (20 grams) and boric acid (60 grams) are intimately mixed and heated to partial fusion. The cold mass is powdered, mixed with α-naphthol (14 grams) and boric acid (10 grams), and heated to 180° for one and a half hours. The black, pasty mass is extracted with boiling water and the residue with boiling dilute aqueous sodium hydroxide; the alkaline extract is acidified, the precipitated acid collected and repeatedly boiled with water and calcium carbonate as long as the filtrate yields a precipitate on acidification. The united filtrates are acidified with hydrochloric acid, the precipitate collected and crystallised from methyl alcohol, which deposits pale yellow prisms melting at 250—252°:

0·1076 gave 0·2690 CO_2 and 0·0461 H_2O. C = 68·18; H = 4·76.

$C_{20}H_{16}O_6$ requires C = 68·18; H = 4·54 per cent.

The acid dissolves in sulphuric acid forming an orange solution which on heating or treating with fuming sulphuric acid turns violet.

The solution, when poured into water, deposits a reddish-brown solid, which is purified by washing on a filter with hot water, drying on porous porcelain, and crystallising from nitrobenzene. The analysis indicates that the substance is a trihydroxymonomethoxynaphthacenequinone:

0·1091 gave 0·2710 CO_2 and 0·0380 H_2O. C = 67·74; H = 3·87.
0·0798 „ 0·1985 CO_2 „ 0·0270 H_2O. C = 67·84; H = 3·76.

$C_{19}H_{12}O_6$ requires C = 67·85; H = 3·57 per cent.

This *trihydroxymonomethoxynaphthacenequinone* forms a dark red powder which melts indefinitely at 260°. It dissolves in alkalis with a bluish-red colour.

2 : 6-*Dicarboxybenzoyl*-1 : 5-*dihydroxynaphthalene*,

$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_{10}H_4(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$.

—This acid is obtained, although only in small yield, by heating 1 : 5-dihydroxynaphthalene (12 grams) with an excess of phthalic anhydride (50 grams) in presence of boric acid (100 grams). The boric and excess of phthalic acids are extracted from the product with boiling water and the residue boiled with sodium carbonate. On acidifying the alkaline extract, a yellow precipitate is obtained, which is a mixture of the mono- and di-benzoyl acids. The former is removed by repeated digestion with methyl alcohol, and the residue is purified by converting it into the calcium salt by boiling with water and calcium carbonate. The acid is then reprecipitated with hydrochloric acid, well washed with hot water on a filter, and dried on porous porcelain:

0·1298 gave 0·3240 CO_2 and 0·0443 H_2O. C = 68·07; H = 3·79.

$C_{26}H_{16}O_8$ requires C = 68·44; H = 3·51 per cent.

This acid forms a yellow powder which decomposes above 300° without melting. It dissolves in sulphuric acid to a violet solution which on heating becomes first green and finally blue. It dissolves in alkalis with an orange colour.

1 : 4 : 5-*Trihydroxynaphthacenequinone* (?).—This substance is

apparently produced when the foregoing acid is condensed by means of boric acid and fuming sulphuric acid. The product is poured into water, the red precipitate washed on a filter with hot water, dried, and extracted with methyl alcohol in a Soxhlet apparatus in order to remove some sulphonic acid which is formed. The residue is crystallised from nitrobenzene, from which it separates as an orange powder which does not melt below 360°:

0·1123 gave 0·2888 CO_2 and 0·0358 H_2O. C = 70·13; H = 3·54.
$C_{18}H_{10}O_5$ requires C = 70·58; H = 3·26 per cent.

This *trihydroxynaphthacenequinone* dissolves in concentrated sulphuric acid and in cold sodium carbonate, yielding cornflower-blue solutions.

1 : 5-*Dihydroxynaphthacenequinone.*—This quinone is prepared by dissolving 1′ : 5′-dihydroxy-2-β-naphthoylbenzoic acid together with twice its weight of boric acid in concentrated sulphuric acid and carefully adding fuming sulphuric acid until a sample of the mixture on pouring into water and making alkaline gives a cornflower-blue solution.

The product is poured into water, the precipitate washed with hot water on a filter, dried, and extracted with methyl alcohol in a Soxhlet apparatus. The residue is then crystallised from nitrobenzene:

0·1576 gave 0·4248 CO_2 and 0·0504 H_2O. C = 73·51; H = 3·58.
$C_{18}H_{10}O_4$ requires C = 74·48; H = 3·44 per cent.

1 : 5-*Dihydroxynaphthacenequinone* forms a brick-red powder which does not melt, but sublimes, below 300°. It dissolves in hot sodium carbonate with a cornflower-blue, and in concentrated sulphuric acid with a bluish-green, colour.

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CLII.—*The Chemical Action of Radium Emanation. Part II. On Solutions Containing Copper, and Lead, and on Water.*

By Alexander Thomas Cameron, M.A., B.Sc., and Sir William Ramsay, K.C.B., F.R.S.

The results of preliminary experiments relating to the action of radium emanation on water form the subject of the previous memoir (this vol., p. 931). It will be remembered that excess of hydrogen above that yielded by the decomposition of water was always found. With the view of accounting for its origin, and with the idea that this *pseudo*-electrolysis, if applied to a copper salt, would give a deposit of metallic copper equivalent to the hydrogen, a solution of copper sulphate was treated with radium emanation in the manner described below. No copper was deposited; and on investigating the products, it was found that a trace of lithium was present in the copper solution along with a considerable amount of sodium. This experiment was carried out during the summer of 1906. The result was so unexpected that it was repeated during the autumn of that year and again in the spring of 1907, always with the same result. A solution of lead nitrate was also exposed to the action of emanation obtained as the maximum yield from 87·7 milligrams of radium as bromide and sulphate. And more recently, a prolonged experiment has been carried out on a specimen of copper nitrate, prepared from electrolytic copper with specially pure nitric acid, avoiding the use of glass as much as possible; the result was substantially the same, for a residue was obtained consisting chiefly of sodium salts, but showing the spectra of calcium and lithium. Simultaneously, a blank experiment was made with the same copper nitrate, leaving it to stand in a glass bulb under identical circumstances, but untreated with emanation. A second blank experiment was also made in which distilled water was treated with emanation with the view of excluding the formation of lithium from a possible alteration in the water, or in the glass of the bulb which contained the reacting substances.

No definite results have been obtained as yet from the experiment with lead nitrate, except that the minute residue after removal of lead from the solution consisted solely of sodium and calcium salts; it did not show the lithium spectrum. The glass of the bulbs employed contained both sodium and calcium; it was free from lithium.

From dry radium emanation, decomposing spontaneously, the inactive gas produced showed a brilliant spectrum of helium; it is possible that a trace of neon was present, but this is uncertain. A bright helium tube, which was exhibited to the Chemical Society in April, left no doubt that by far the major part of the inactive gas resulting from the dry emanation consists of helium.

The gas proceeding from the action of the emanation on a saturated solution of slightly acid copper nitrate was also analysed; it contained a large percentage of nitric oxide, and left a residue of 0·3 c.c. of nitrogen. This gas, when examined spectroscopically, contained argon, but no helium.

The gas, similarly collected from water on which emanation had acted, when examined spectroscopically, after removal of ordinary gases, showed a brilliant spectrum of neon, in which all the visible lines of neon were identified by comparison with a neon tube. This gas also contained a trace of helium; the green, yellow, and red lines were feeble; the blue lines and the violet line were invisible, owing to the small quantity of helium present.

EXPERIMENTAL.*

First Experiment, with Copper Sulphate.—A specimen of ordinary "pure" copper sulphate was recrystallised four times. A saturated solution of this salt was treated in a small soda-lime-glass bulb with emanation from radium bromide (152 milligrams) and sulphate (10 milligrams), containing 87·7 milligrams of metal, on the suppositions that the atomic weight of radium is 225, that the bromide crystallises with 2 molecules of water, and that the sulphate is anhydrous. Only one dose, collected during four days, was introduced, corresponding to about 0·3 cubic millimetre of emanation. After standing for more than a month, the copper was removed from the treated solution with hydrogen sulphide, and the residue, after evaporation, consisted mainly of sulphates of sodium and calcium, the latter present in very small amount; it showed the red line of lithium when examined spectroscopically. The original specimen of copper sulphate, from which the crystallised sample used for the experiment had been prepared, was then examined in the same way; it was found to contain a trace of lithium. The recrystallised sample failed to show this test.†

Second Experiment, with Copper Sulphate.—For this experiment, the copper sulphate was produced by dissolving metallic

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* To save space, the description of the precautions taken during the first three experiments has been abbreviated; details relating to the fourth experiment are alone given.

† Mr. A. C. Egerton has been so obliging as to carry out a series of crystallisations of copper sulphate to which a small known quantity of lithium sulphate had been added. It was of interest to determine whether the double sulphate, $CuLi_2(SO_4)_2,6H_2O$, could be easily separated from excess of copper sulphate by crystallisation. Two sets of experiments were made, in which both copper and lithium were determined in the first four fractions of a mixture of copper sulphate with a trace of lithium nitrate. The results are :

		Fraction 1.	2.	3.	4.
I.	Copper...	0·760 gram	0·827 gram	0·843 gram	0·823 gram as metal.
	Lithium.	trace	0·0001 ,,	0·0007 ,,	0·0015 ,, as sulphate.
		Fraction 1.	2.	3.	4.
II.	Copper ..	0·7008 gram	0·5065 gram	0·6426 gram	0·6401 gram as metal.
	Lithium.	0·0001 ,,	0·0004 ,,	0·0008 ,,	0·0029 ,, as chloride.

It appears unlikely, therefore, that, after four recrystallisations of an ordinary sample of copper sulphate, any lithium could be found in the recrystallised sample.

copper, deposited from the sulphate with a current of three volts potential, in sulphuric acid, which had been specially made in the laboratory for the purpose by the "contact" process. Glass vessels were used, but a careful analysis of the glass, in which the amyl alcohol method of separating lithium as chloride from the other alkalis was employed, failed to reveal the presence of lithium in it.

The same process was adopted, the amount of emanation introduced having been the same. After more than a month, the bulb was opened and its contents analysed, and again with the same result. The residue of sulphates weighed 1·1 milligrams; it gave a brilliant sodium spectrum, and it again showed the red line of lithium.

Third Experiment, with Copper Nitrate.—The copper sulphide obtained from experiment 2, after solution in nitric acid, was converted into acetylide with hydroxylamine hydrochloride, ammonia, and acetylene. This was the method employed to separate copper from all other metals of the sulphide group. The copper acetylide was dissolved in dilute nitric acid in a platinum basin, and the nitrate was evaporated to dryness. It was then dissolved in water and exposed to five doses of emanation, amounting in volume to 1·5 cubic millimetres. The solution was then allowed to stand for forty-one days, when practically all the emanation must have changed. The copper nitrate deposited a trace of basic salt. At the end of that time, all the nitrate was washed out of the bulb into a platinum basin, the purest obtainable water, kept in a steamed-out glass wash-bottle, being used, and a current of hydrogen sulphide, led in through a platinum tube, was used to throw down the copper. The filtrate from the copper sulphide was evaporated to dryness in a platinum basin and ignited; it weighed 2·48 milligrams. The spectrum was chiefly that of sodium, but the lithium red line was detected, and its position confirmed. It was undoubted.

The copper sulphide was dissolved in nitric acid, and the copper was precipitated as before in the form of acetylide (Erdmann and Makowka, *Zeitsch. anal. Chem.*, 1907, **46**, 128). The filtrate was dried and ignited to decompose salts of hydroxylamine; only a trace of iron was found in it, due probably to the acids employed.

Fourth Experiment, with Copper Nitrate.—During this experiment, the greatest care was taken to avoid the introduction of any possible impurity. The vessels used, with exception of the original bulb and of a glass pipette, were of platinum and silica. Only gaseous reagents were used in the whole work, up to obtaining the residue of alkali.

The source of the copper was "pure" laboratory copper sulphate; it was dissolved in distilled water, of which 20 c.c. gave a total unweighable residue. This solution was electrolysed, the current used being 1 ampere, and the E.M.F. 3 volts, and it was deposited on a rotating cathode of smooth platinum. After two and a half hours, the copper coating was washed several times with the purest water.

Pure redistilled nitric acid was the solvent for the copper; the residue from 50 c.c. weighed 0·4 milligram. About half the copper was dissolved; the solution was evaporated to dryness in a platinum basin over a water-bath, and the residue was heated for two hours longer to expel the last traces of nitric acid. This copper nitrate was dissolved in pure water and filtered into two glass bulbs, newly made from the same piece of tubing. One was exhausted and sealed (I); emanation which had collected for ten days was introduced on April 29th into the other bulb (II); emanation was again added on May 4th, 9th, and 14th. The bulb was then sealed off. The total quantity of emanation introduced was approximately 1·62 cubic millimetres.

After the first day, a slight cloudiness appeared in bulb II, whereas the contents of I were perfectly transparent. On the second day, the liquid in II was distinctly green, whilst the copper nitrate in I, naturally, remained clear blue. The green colour did not become more intense.

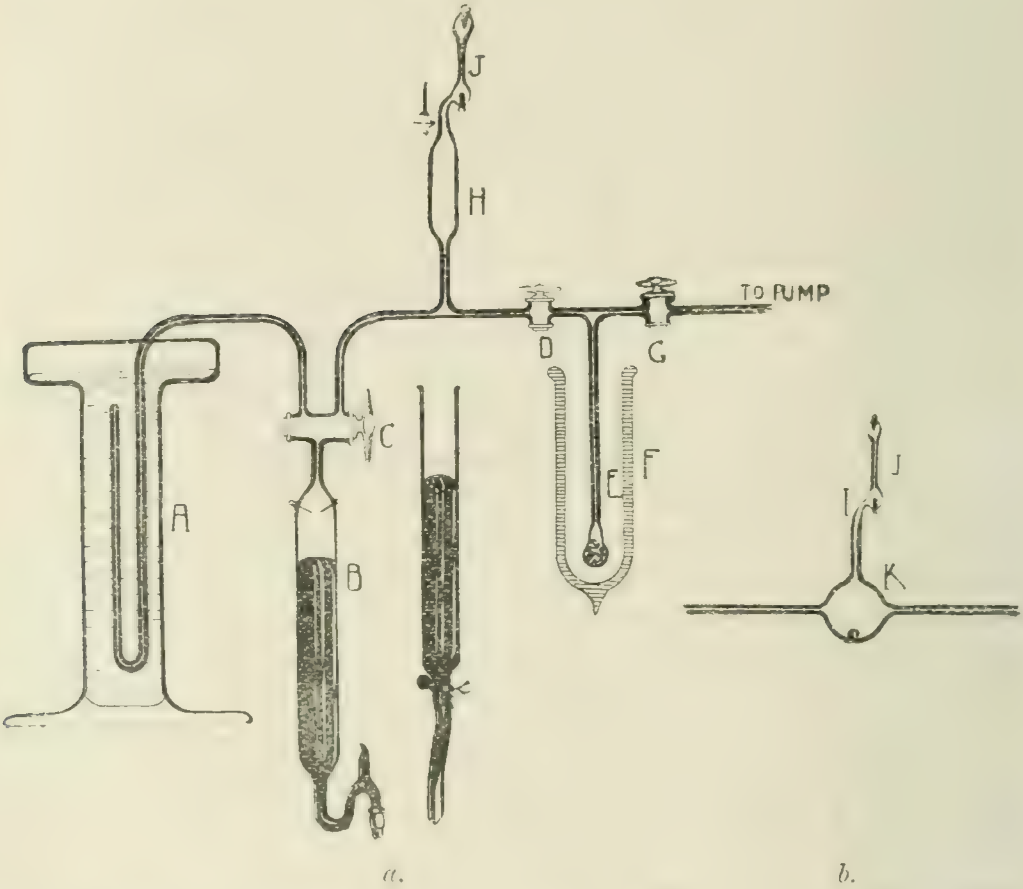
The residual gas from the emanation was collected as "copper gas." The method was: to freeze with liquid air the contents of the bulb, then to open the tap to the pump, and to evacuate the bulb; this yielded the "copper gas." Emanation with some hydrogen was then introduced into the bulb; the hydrogen was then pumped out, and examined subsequently. It may be stated here that this gas was used as a source of helium; it is possible that, when freshly prepared, some neon lines were present, but this is not certain.

Both bulbs were finally opened on June 10th; from the untreated bulb nothing could be pumped off, as might have been supposed.

In order to gain some knowledge of the action of the emanation on glass alone, a similar bulb was charged with pure distilled water, and emanation was introduced on May 22nd and 29th, and on June 7th and 11th; in all, 1·44 cubic millimetres were added. The bulb was opened on June 29th. The liquid contents of the bulbs are left for after consideration; the gaseous contents alone will be now treated of.

Investigation of the Gaseous Products.—A curious circumstance now transpired. On pumping out the gaseous contents of the bulb containing copper nitrate (the "copper gas") for the last time, it was naturally collected in the same tube into which it had previously been introduced; but the copper solution was not frozen with liquid air, in order that *all* gases might be removed, and not merely those volatile at the lower temperature. On mixing, red fumes were observed; the explanation evidently is that the nitric oxide, to which the nitrate ion had been reduced, had been frozen during the former extractions of gas, and had accumulated in the bulb. It is known that nitric oxide forms unstable combinations with copper salts, and these, at the low temperature of liquid air, must have remained undissociated. This mixture of gases was then well shaken with mercury, in order to absorb the nitric peroxide, and the analysis of the residual gas was carried out. The deposit of mercurous nitrate was then treated with concentrated sulphuric acid, and the nitric oxide was thus liberated. In this manner, the analysis of the gaseous mixture was rendered complete.

Fig. 1.



a. *b.*

The method of separating and examining the inactive gases was as follows. After the carbon dioxide had been removed with potassium hydroxide, sparks were passed, and the hydrogen and oxygen, or carbon monoxide and oxygen, were made to unite. The residue was again treated with potash, so as to absorb any carbon dioxide formed from carbon monoxide. If necessary, this operation was repeated after a measured quantity of oxygen had been added. The oxygen was then absorbed by phosphorus, and the residue of nitrogen was introduced through the inverted siphon, *A*, Fig. 1 (*a*), into the burette, *B*. The rest of the apparatus was connected with the pump through *G* and evacuated; *G* was then closed. The stopcock, *C*, was then opened, and the gas under examination was allowed to enter, the mercury being raised just above the stopcock, which was then closed. The bulb, *E*, containing charcoal, previously heated to 230° in quinoline vapour and freed from adsorbed gases, was then cooled with liquid air; any argon and nitrogen present was condensed in *E*. A paper cup was then constructed round the tube, *H*, moistened with water, and, on pouring in liquid air, a vessel of ice was produced; by this means the tube, *H*, was cooled, so that the major part of the gas which had not condensed in the cooled charcoal was contained therein. The tap, *D*, was then closed, and mercury was forced up through *C* to the point *I*; here again a similar funnel of wet paper was constructed and charged with liquid air, so that, in sealing off, mercury vapour should be condensed, and should not give its spectrum in the vacuum tube. The vacuum tube, *J* (which had at the beginning of the operation been glowed out to remove hydrogen from the electrodes), was then sealed off.

The stopcock, *G*, was then opened, and the gas was pumped off; the charcoal was again surrounded by boiling quinoline, so as to make certain of extracting all the gas. Oxygen was added to the nitrogen, and by sparking in presence of potassium hydroxide, all nitrogen was removed. The gas was then admitted into a piece of apparatus similar to that already described, but differing, inasmuch as, instead of charcoal, phosphorus was placed in *K* to absorb the oxygen, the only residual gas besides those of the inactive group. After absorption of oxygen, mercury was allowed to enter and force the residual gas up into the little vacuum tube, where its spectrum could be examined after condensing mercury vapour as before.

The gases from the various solutions were examined as described. Their composition was:

	From copper nitrate solution, "treated."	From "treated" water.	From "treated" lead nitrate.
Nitric oxide, NO	1·12 c.c.	—	—
Nitrogen, N_2	0·34 ,,	0·307 c.c.	0·032 c.c.
Carbon dioxide, CO_2...	0·27 ,,	0·065 ,,	0·009 ,
Carbon monoxide, CO.	— ,,	0·030 ,,	— ,
Hydrogen, H_2	0·44 ,,	3·746 ,,	0·184 ,,
Oxygen, O_2...............	1·12 ,,	1·562 ,,	0·700 ,,
	3·29 ,,	5·710 ,,	0·925 ,,

From the residue of nitrogen from the gas evolved by the emanation by its action on copper nitrate, the residual nitrogen was removed by sparking with oxygen over sodium hydroxide, and the excess of oxygen was removed, as already described, with phosphorus in the apparatus shown in Fig. 1 (*b*). The spectrum was that of pure argon; no helium or neon line could be observed. It must be noticed, however, that two red lines, of approximate wave-length 6739 and 6670, were observed, which were not present in the argon spectrum used for comparison. Now it is possible that air might have leaked in through the stopcocks, for the emanation was introduced during a period of fifteen days, and the bulb was then sealed off. But if the argon had been derived from the atmosphere alone, helium should still have been visible in the spectrum if it had been derived from the emanation; reckoning the nitrogen as entirely atmospheric, the corresponding amount of argon would have been approximately three cubic millimetres, and we know, from experiments on the emanation above that from 1·62 cubic millimetres of the emanation, the volume of helium to be expected should have been about 5 cubic millimetres, a quantity easily visible in the presence of so little argon. We regard it as more probable that there was no leakage, and that the nitrogen was derived from the copper nitrate. This point, however, cannot be regarded as settled until further experiments have been made, in which the possibility of leakage of air into the apparatus is completely excluded.

The gas from the water, treated with emanation, was examined by the help of cooled charcoal. The uncondensable gas, forced up into the small vacuum tube, gave a brilliant neon spectrum in which the helium spectrum was faintly visible. A comparison was made with a vacuum tube containing atmospheric neon, and every line of neon was identified in the gas from the "treated" water. With a helium tube for comparison, it could be seen that the yellow and green helium lines of wave-lengths 6677, 5876, and 5016 were present, but the other lines of helium were too faint to be visible. There were also other lines present, of which the approximate wave-lengths are:

Red	6242	strong	
	6223	feeble	
	6149	,,	
Yellow	6018	,,	
	5912	,,	
Yellow-green	5828	very feeble	
,,	5806	,,	
,,	5720	,,	
Green	5454	,,	$(Hg=5461)$
,,	5259	feeble	
,,	4893	very feeble	$(H_2=4861)$
,,	4625	,,	

As the gas from the lead nitrate was the product of only one dose of emanation, it was not thought worth while to examine the inactive residue. That must be left for further experiment.

Investigation of the Copper Nitrate.—Parallel experiments were carried out with the "treated" nitrate, and with a sample of the same solution, filtered into a bulb of similar glass, which was pumped empty and allowed to stand for the same length of time as the bulb containing the nitrate plus emanation. These will be termed I. and II. respectively.

I. contained a greenish-white deposit; II. was quite transparent. The mixed solid and liquid from I. were transferred to a weighed silica tube, which was constructed for centrifugalisation, and centrifugalised. The liquid was poured into a platinum crucible. The solid was twice washed with pure water* and the washings were added to the contents of the crucible. The residue, dried at 130°, weighed 4·11 milligrams. This residue was dissolved in nitric acid, distilled directly from a glass flask through a platinum tube sealed into the flask; it gave a blue solution. The nitric acid, thus prepared, gave no perceptible residue on evaporation. The acid solution was diluted with distilled water, and hydrogen sulphide, which had been allowed to stand for some hours in the Kipp's apparatus, was passed in through a platinum tube. A black precipitate was produced, which, with the liquor, was added to that obtained from the rest of the copper nitrate.

The liquid from the greenish-white precipitate, which was mainly a basic nitrate of copper, was also treated with hydrogen sulphide, using the same precautions as before. The precipitate of sulphides was separated by centrifugalisation in a silica tube, but a new glass pipette was used to transfer the supernatant liquid to a platinum capsule. The process was repeated so as to ensure the separation of all sulphide.

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* This water, which had also been used in the preparation of the copper nitrate and for treatment with emanation, was prepared as follows:—Ordinary distilled water was redistilled, using a tin condenser, into a Jena-glass flask. It was then frozen, being violently shaken in the shaking machine. Half the ice was allowed to melt and drain away, and the residue, when liquid, was stored in steamed-out Jena flasks. Previous to the copper nitrate analysis, 20 c.c. of this water gave a just visible total residue, absolutely unweighable, and invisible after ignition. The residue on evaporation, after the water had stood during the time required for the analysis, was perhaps perceptibly greater, but was still quite negligible.

The filtrate was evaporated nearly to dryness on a water-bath, and finally dried over a flame. The residue was dissolved in four drops of water, and transferred to a smaller capsule. Four drops and five drops of the purest redistilled water were successively used as wash-water; the solution was evaporated over a small glass water-bath, and finally dried at 130°. The capsule was transferred while still hot to a glass weighing-dish. The weight of the residue was 1·67 milligrams. Its spectrum consisted of sodium (very strong) and calcium (present, but weak), and the lithium red line was identified and compared with the spectrum of lithium chloride. The position of the line was undoubted. A mixture of sodium and lithium chlorides was made, so as to be able to estimate approximately the percentage of lithium present. When the lithium was present in such amount that it formed 0·01 per cent. of the sodium, the intensity of the lithium red line was comparable with that of the residue from the copper nitrate. The total quantity of lithium therefore may be estimated as 0·00017 milligram.

II. The blank experiment was treated in exactly the same manner. The residue weighed 0·79 milligram. The spectrum was that of sodium (very strong) and calcium (feeble); no trace of the lithium line could be observed. This was again repeated with identical results.

I. The copper sulphide was heated in a clean glass beaker with pure distilled hydrochloric acid. As there was now no necessity to exclude alkalis, ordinary distilled water and glass vessels were used. The precipitate dissolved, leaving a small residue of sulphur. The liquid was filtered into an Erlenmeyer flask, and ammonia was blown in until the cupric hydroxide, precipitated at first, had re-dissolved. Crystals of hydroxylamine hydrochloride were then added, and the solution was warmed; when it had become quite colourless, acetylene was passed in for some minutes. The cuprous acetylide was filtered off, and the process was repeated; the solution gave no further precipitate, even after standing overnight. The filtrate from the acetylide gave no precipitate with hydrogen sulphide, but, on acidifying with hydrochloric acid, a faint precipitate was produced, consisting largely of sulphur. This residue was digested with *aqua regia*; the solution gave no blue coloration with ammonia; it was evaporated to dryness, dissolved in hydrochloric acid, evaporated, and taken up with a drop of water. It gave a minute, black precipitate with hydrogen sulphide, too small for further investigation.

The copper acetylide was transformed into sulphate, and weighed as such. The weight corresponded to 0·815 gram of $Cu(NO_3)_2$, which was therefore the amount treated with emanation.

II. The blank experiment was treated in an exactly similar manner; the only difference was that in this case no trace of a black precipitate could be produced in the filtrate from the copper acetylide. The weight of nitrate taken was 0·968 gram of $Cu(NO_3)_2$. The black precipitate, if it is possible to produce it in greater amount, deserves investigation.

Investigation of the Lead Nitrate.—Here again a duplicate, untreated sample was examined along with the sample which had been exposed to the action of the emanation. As before, the treated sample will be termed I., and the untreated sample II.

I. The treated sample was transferred to a platinum crucible; the glass bulb was twice washed out with the purest distilled water;* dilute sulphuric acid, produced in the laboratory by the contact process, and uncontaminated by alkali, was added, until no further precipitate fell. The precipitate was separated by centrifugalisation in a silica tube, and the sulphate residue was transferred to a glass beaker.

The liquid was transferred to a platinum capsule, and evaporated to dryness to remove sulphuric acid; water was added, and hydrochloric acid was then distilled in, in the state of gas. Hydrogen sulphide was then passed in, and the black precipitate of sulphide was centrifugalised. The liquid was decanted into a platinum capsule, and evaporated to dryness on a water-bath. Water was again added, hydrochloric acid again distilled in, and then ammonia was blown through the solution. There was a very slight reddish-brown precipitate, resembling ferric hydroxide. This was removed centrifugally in silica, and the solution was poured into a platinum capsule. This liquid was evaporated, and heated to volatilise ammonium salts. The residue weighed 0·45 milligram, but some had previously been removed for spectroscopic testing; the original weight was probably about 0·6 or 0·8 milligram. The spectrum was that of sodium only; no calcium or lithium was visible.

The reddish-brown precipitate gave the reactions of iron.

II. The blank experiment gave precisely similar results so far.

I. The precipitate of lead sulphate was dissolved in sodium hydroxide prepared from sodium with alcohol. (Iron was present as an impurity in this sodium hydroxide.) There remained a very small insoluble residue, distinct from the flocky precipitate of ferric hydroxide; the latter dissolved in hydrochloric acid, but some grains of a black powder remained. This was not observed in II.; the ferric hydroxide dissolved completely and at once.

I. The precipitate of lead sulphide, obtained by passing hydrogen sulphide through the liquid from which the sulphate had been separated centrifugally, was dissolved by saturating the liquid with hydrogen chloride and heating. There remained a residue of six-sided, colourless tables, and some reddish-yellow grains. The whole liquid was evaporated to dryness, when lead chloride separated. Alcohol was added, and the lead chloride was separated centrifugally. The alcohol was evaporated in a silica capsule over a water-bath. The residue of white crystals still was seen, and also a yellow powder similar to that already described. Experiments made with the blank, II., gave no crystals and no yellow grains.

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* The wash-bottle was wholly of glass; no grease was used, and the flask was thoroughly steamed-out before the specially pure distilled water was introduced.

The residues, both from the copper and from the lead, are unfortunately so small that their investigation is exceedingly difficult. It is our intention to try to produce them in larger amount by using larger quantities of emanation and by employing a silica bulb. The latter is already in operation, and by its means the objections naturally attaching to glass bulbs will be removed. These experiments must be considered as preliminary. It is necessary first to find out where to search for the unknown before proper experiments can be made.

Examination of the Water treated with Emanation.—After exposure to the action of 1·422 cubic millimetres of emanation, the water, after gases had been removed, was shaken in the bulb with freshly distilled, pure ether. The ether was tested for hydrogen peroxide with titanium sulphate, and a yellow colour showed its presence in small amount. This contradicts the observation previously made, when the water was allowed to evaporate into phosphorus pentoxide and gave no gas; it might have been supposed that hydrogen peroxide would have been decomposed during such evaporation. It is possible, however, that it is absorbed by phosphorus pentoxide when its vapour slowly comes in contact with the anhydride.

The remaining water was evaporated to dryness in a platinum capsule; the residue was somewhat deliquescent; it weighed 0·71 milligram. The residue gave the spectrum of sodium (strong) and potassium (very faint), but no lithium.

It is to be inferred that the alkali residue, obtained from the blank copper and lead experiments and from the glass, all having approximately the same weight, is derived from the glass bulb. The greater weight of the residue of alkali salt from the treated copper nitrate may be noted. It can hardly be fortuitous, but some experiments with the silica bulb will show whether this excess is real and not a chance occurrence.

Discussion of Results.—That the radium emanation, during its spontaneous change, parts with an enormous amount of energy, has already been emphasised in this series of papers. It has been suggested that this energy is due to the explosive emission of "α-particles," which may conceivably be identical with helium. Whether this last supposition be just or not, these particles may certainly be regarded as small masses of molecular dimensions moving with a very high velocity. It may be taken that, since the emanation presents a strong resemblance to the inactive gases of the argon series in the character of its spectrum, and in its indifference to chemical reagents, it belongs in all probability to that series, and we have already suggested that its atomic weight may be approximately 216·5. When left alone in an otherwise vacuous vessel, or when mixed with oxygen and hydrogen gases, it is known to yield helium as one of its products. This was first shown by Ramsay and Soddy, and the observation has been confirmed by Indrikson, by Debierne, by Giesel, by Curie and Dewar, and by Himstedt and Meyer.

It now appears that when dissolved in water, it yields almost exclusively neon as its gaseous educt; the trace of helium observed is produced, in all probability, from the undissolved and gaseous portion of the emanation. When a copper salt is simultaneously present in solution, helium, if present at all, cannot be detected, and argon is the main product, mixed possibly with a trace of neon. It may be contended that the argon formed in presence of copper sulphate is derived from atmospheric nitrogen which may have leaked in through the stopcocks. It is impossible at this stage to disprove this possibility, but the presence of argon does not account for the absence of helium, and it is remarkable that the amount of nitrogen is almost exactly the same both when water and when copper sulphate were present, although the conditions were by no means parallel.

We suggest (1) that helium and the α-particle are not identical; (2) that helium results from the "degradation" of the large molecule of emanation by its bombardment with α-particles; (3) that this "degradation," when the emanation is alone or mixed with oxygen and hydrogen, results in the lowest member of the inactive series, namely, helium; (4) that if particles of greater mass than hydrogen or oxygen are associated with the emanation, namely, liquid water, then the "degradation" of the emanation is less complete, and neon is produced; (5) that when molecules of still greater weight and complexity are present, as is the case when the emanation is dissolved in a solution of copper sulphate, the product of "degradation" of the emanation is argon. We are inclined to believe, too, that (6) the copper also is involved in this process of degradation, and is reduced to the lowest term of its series, namely, lithium; at the same time, inasmuch as the weight of the residue of alkali, produced when copper nitrate is present, is double that obtained from the blank experiment, or from water alone, the supposition is not excluded that the chief product of the "degradation" of copper is sodium. It may be argued in favour of this view that, inasmuch as sodium is a much commoner element than lithium, it may be regarded as more stable, and therefore more likely to be produced.

It is to be noticed that the sodium "produced" from copper, if this suggestion is correct, corresponds to an enormously greater number of molecules than the helium. That is true, but it must be remembered that the chances of collision of a molecule of "disrupting" emanation with an atom of copper are almost infinitely greater than with one of its own atoms, because the number of copper ions in the solution is considerable.

Experiments confirmatory of the above view, in which it appears that an acid solution of thorium nitrate continuously produces carbon dioxide, are in progress. The observation has been made three times, at intervals of six months between the observations, but publication of an account of these experiments will be delayed until a fourth experiment has been made and a corresponding blank experiment has been studied.

It is evident that the research, of which the foregoing is a description, is merely a preliminary survey of the field to be explored, and that much work must be done before the tentative hypothesis which has been put forward can be substantiated.

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CLIII.—*Molecular Aggregation in Solution as Exemplified in Aqueous Mixtures of Sulphuric Acid with Inorganic Sulphates.*

By JOHN HOLMES and PHILIP JOHN SAGEMAN.

IN a recent communication by one of us (Holmes, Trans., 1906, **89**, 1774) an attempt was made to deduce the degree of aggregation of the molecules of mutually miscible liquids from a consideration of the volumetric changes yielded by different mixtures. Assuming that the free path of a liquid molecule can be represented by a spherical surface, and also that each molecule contains a fixed amount of energy, which is analogous to electrical energy, and results in forces of repulsion or attraction for other molecules according to their nature, the deduction was made that the percentage change in volume resulting from the co-mingling of equal numbers of dissimilar molecules, when split up in proportion to the so-called molecular volumes, will, in the case of the molecules occupying the greater volume, yield a factor which is greater for this mixture than for other simple molecular mixtures.

Now if in a mixture of liquids miscible without change in the chemical nature of their molecules the changes in volume were merely the resultant of the forces peculiar to each set of molecules, the maximum deviation from the theoretical would necessarily occur when the molecules are mixed together in equal proportions, and, in fact, from a determination of the difference in volume yielded by any particular mixture, it would be possible to calculate the effect for all other mixtures from the expression:

$$\xi = a(100 - a)K,$$

where ξ is the change in volume and a the percentage of one set of molecules in the mixture.

There are, however, two other factors which influence what may be called this normal change in volume, namely, (1) the difference in the relative weights of the molecules, which from the circumstance that there are spaces between the molecules (*loc. cit.*) results by gravitation in a closer fitting in, and (2) the difference in the relative volumes or influential spheres occupied by the molecules, which again allows of further close-packing as this difference increases. These factors, acting in conjunction, tend, when the normal change in volume is relatively small, seriously to vitiate conclusions which otherwise might be drawn from a consideration of the mixtures at which this maximum change occurs, and it is probable that liquids will be found the molecules of which have a repelling action on each other, but which by reason of these disturbing influences of mass and volume predominating over the normal repulsive forces in some mixtures will afford both contractions and repulsions at different concentrations. The effect of these influences on the degree of contraction occurring in aqueous mixtures of similarly aggregated liquids, which have approximately the same molecular volume compared with that of water at the same temperature as unity, but differing in density, is shown in the following instances, calculated from data quoted in the above paper.

Column I shows the percentage of water-molecules in the mixture, and

Columns II*a* and II*b* the contraction in c.c. when 100 gram-molecules of the active constituents of the mixture are present:

I. Percentage.	II*a*.—Ethyl alcohol. Density at 15·5°/15·5° = 0·7940. Molecular volume = 3·22. c.c.	II*b*.—Acetic acid. Density at 20°/4° = 1·0497. Molecular volume = 3·17. c.c.
11·1	41·8	50·8
16·7	63·9	70·1
25·0	79·4	92·6
33·3	93·3	101·4
40·0	103·1	108·1
50·0	110·0	113·2
60·0	112·4	111·4
66·7	110·1	103·7
75·0	102·1	90·9
83·3	82·4	71·7
88·9	58·6	53·6

I. Percentage.	II*a*.—Methyl alcohol. Density at 15·5°/15·5° = 0·7956. Molecular volume = 2·27.	II*b*.—Formic acid. Density at 20°/4° = 1·2213. Molecular volume = 2·09.
16·7	52·7	20·4
25·0	69·7	29·4
33·3	85·6	37·2
40·0	92·3	43·6
50·0	99·2	49·0
60·0	96·3	49·7
66·7	88·6	47·6
75·0	73·7	42·4
83·3	51·6	32·0

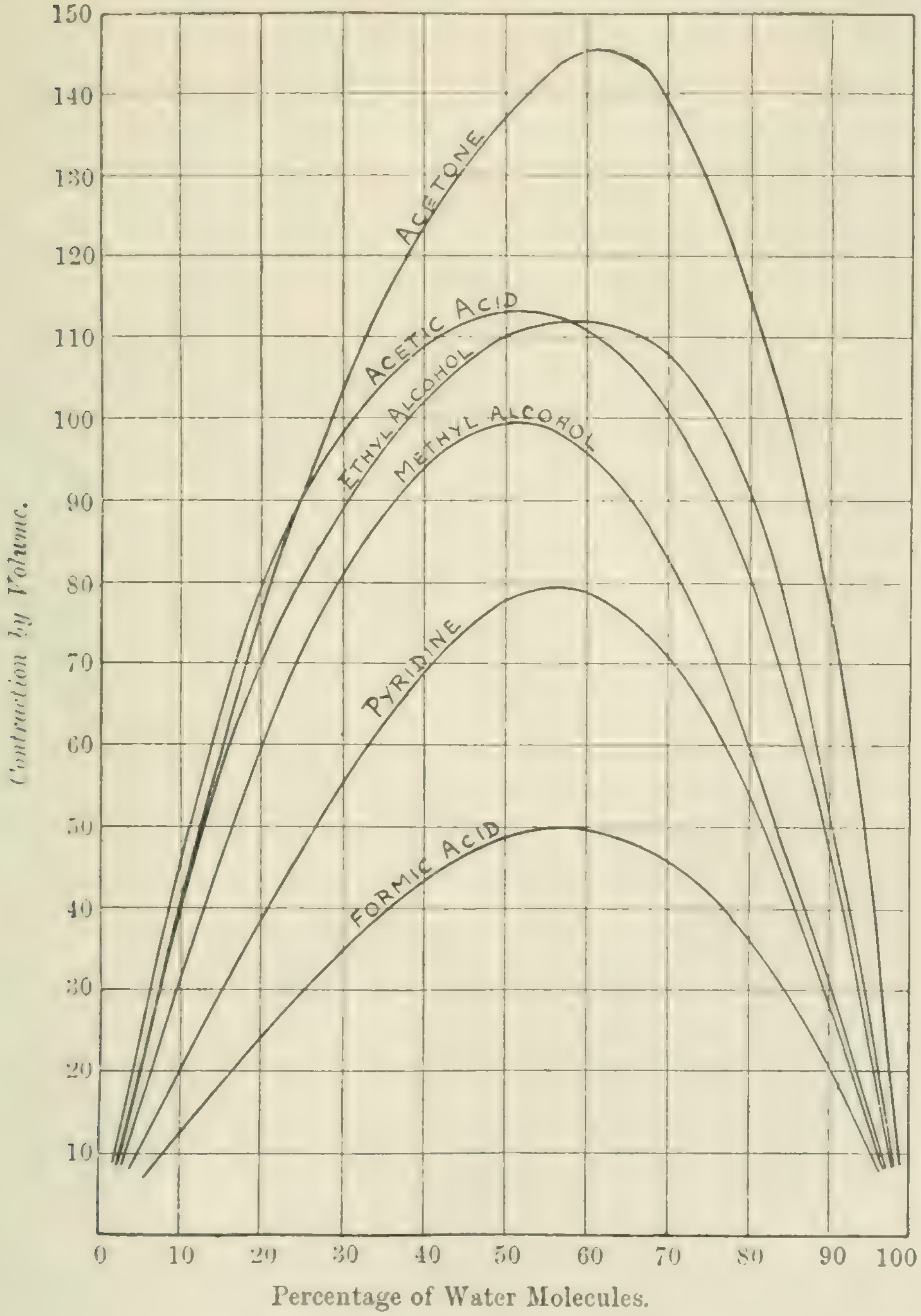
I. Percentage.	II*a*.—Pyridine. Density at 15·5°/15·5° = 0·9880. Molecular volume = 4·41.	II*b*.—Acetone. Density at 20°/4° = 0·7920. Molecular volume = 4·04.
16·7	33·4	65·3
25·0	46·8	90·7
33·3	59·8	111·4
40·0	68·7	123·1
50·0	78·1	135·6
60·0	79·1	145·4
66·7	74·7	143·7
75·0	63·5	128·8
83·3	47·4	105·1

The effect of the weight of the molecule and the apparent volume it occupies is more readily seen from the curves (Fig. 1), and it is evident that in the absence of any method of eliminating these disturbing influences in such mixtures as chloroform and ether, carbon disulphide and ethyl alcohol, &c., in which the influence of mass is considerable, deductions regarding molecular complexities cannot, with any degree of accuracy, be based upon such data.

In the present communication, we give the results of a study of the interaction of molecules under conditions in which the influences of mass and volume are to a large extent eliminated.

It is common knowledge that when sulphuric acid is mixed with water, a considerable contraction in volume occurs. As in the case of the lower alcohols and acids of the paraffin series (*loc. cit.*), it is found that the greatest difference between the percentage of sulphuric acid in the mixture, and the theoretical percentage assuming no contraction, occurs at an admixture representing an equal number of molecules referred to the gaseous state. Sulphuric acid therefore is aggregated similarly to water. The same inference may be drawn from the following contractions in volume which are obtained in mixtures of

FIG. 1.



100 gram-molecules, calculated from Domke and Bein's densities of aqueous sulphuric acid mixtures (*Zeitsch. anorg. Chem.*, 1905, **43**, 125), and in which the great attractive power of the sulphuric acid for water masks, to a large extent, the effect of differences in density near the mixture of equal numbers of molecules.

Columns I and II have the same significance as before:

I.	II.	I.	II.
Percentage.	c.c.	Percentage.	c.c.
11·1	105·8	60·0	299·4
16·7	150·2	66·7	276·9
25·0	208·2	75·0	237·3
33·3	256·4	83·3	184·8
40·0	286·9	88·9	143·5
50·0	310·6		

Relatively concentrated aqueous solutions of the inorganic sulphates also contract on dilution with water. When, however, dilute sulphuric acid is mixed with aqueous solutions of its salts, the volume of the mixture is always greater than the sum of the initial volumes.

Now Ostwald (*J. pr. Chem.*, 1877, [ii], **16**, 385) has demonstrated that when aqueous solutions of many of the common acids and bases are mixed together in equivalent proportions, an expansion in volume occurs. Similar expansions were obtained when dilute sulphuric acid was mixed with solutions of some of its neutral inorganic salts. The similarity of these results suggests that the increase in volume is due to the same cause in each instance, and, although it was found that Guldberg and Waage's law of mass action could not be applied to the latter mixtures, Ostwald arrived at the conclusion that acid salts were produced, but that the yield diminished as the proportion of water is increased.

Again, from the point of view of the dissociation theory of Arrhenius, the sulphuric acid, neutral sulphate, and acid sulphate exist in these mixtures in a partially dissociated condition, and the influence of the concentrations of the undissociated molecules on the change in volume is further modified by the presence of the several free ions (Barnes and Scott, *J. Physical Chem.*, 1898, **2**, 536).

Since aqueous solutions of sulphuric acid and neutral sulphates on dilution with water give contractions in volume which vary with the concentration, it is evident that in any mixture the water present in each solution will influence the other solution. In order to eliminate such influences due to the solution medium, it was decided, as the result of a considerable number of experiments, to mix solutions in which the contractive effect of the salt solution for the water in the sulphuric acid mixture was equivalent to the contractive effect of the sulphuric acid mixture for the water in the salt solutions.

A series of mixtures was made with water and aqueous sulphuric acid having at 15°/15° densities of 1·04992, 1·09503, 1·13557, 1·17911, and 1·22749 respectively, and the contraction curve in each case was plotted with the volume of *water* constant at 100 volumes. Similarly, for each salt solution experimented with, the contraction curves with water were plotted when the volume of the *salt* solution was constant at 100 volumes. In choosing therefore the mixture of sulphuric acid necessary to eliminate within a near approximation to accuracy contractive influences when mixed with a particular salt solution, the salt curve was superimposed on the series of aqueous sulphuric acid curves and that mixture taken the curve of which most nearly coincided; in cases where the curves were not quite of the same order that mixture was chosen the curve of which coincided most nearly at the point of equimolecular mixtures.

The densities of the different solutions and mixtures were taken at 15°/15° in a pyknometer, having a capacity of about 70 c.c., and the changes in volume calculated from the several weights and densities.

For the purpose of calculating the volume of each solution containing an equal number of molecules according to the usual formulæ, and which by reason of the relatively small changes in volume are only required approximately, use was made of Comey's Dictionary of Solubilities for the densities of the several salt solutions, and Domke and Bein's data in the case of aqueous sulphuric acid mixtures (*loc. cit.*).

In the following series of mixtures, Column I represents the volume of aqueous sulphuric acid mixed with 100 volumes of the salt solution, and Column II the expansion by volume thus obtained.

(I.) Mixtures of potassium sulphate with sulphuric acid.

Density of potassium sulphate solution = 1·06907.
" sulphuric acid " = 1·05448.

These solutions contain 88·8 grams of potassium sulphate and 83·5 grams of sulphuric acid per litre respectively; 100 volumes of the salt solution contain the same number of molecules (K_2SO_4) as 59·8 volumes of the acid (H_2SO_4):

I.	II.	I.	II.
7·71	0·082	119·57	0·516
14·93	0·149	178·00	0·550
19·97	0·189	235·58	0·583
29·97	0·261	478·78	0·626
58·63	0·397		

(II.) Mixtures of sodium sulphate with sulphuric acid.

Density of sodium sulphate solution = 1·09506.
" sulphuric acid " = 1·11219.

These solutions contain 112·1 grams of sodium sulphate and 178·9 grams of sulphuric acid per litre respectively:

Equimolecular volumes: $100Na_2SO_4,Aq$: $3·2H_2SO_4,Aq$.

I	II.	I.	II.
5·50	0·114	86·16	0·751
10·88	0·214	129·88	0·816
14·55	0·275	173·12	0·846
21·88	0·381	344·28	0·894
43·12	0·581		

(III.) Mixtures of ammonium sulphate with sulphuric acid.

Density of ammonium sulphate solution = 1·13251.
„ sulphuric acid „ = 1·20884.

These solutions contain 262·4 grams of ammonium sulphate and 341·3 grams of sulphuric acid per litre respectively:

Equimolecular volumes: $100(NH_4)_2SO_4,Aq$: $57·1H_2SO_4,Aq$.

I.	II.	I.	II.
7·27	0·255	114·48	1·566
14·16	0·473	170·85	1·644
19·09	0·614	228·10	1·666
28·57	0·845	453·58	1·738
57·12	1·273		

(IV.) Mixtures of magnesium sulphate with sulphuric acid.

Density of magnesium sulphate solution = 1·11153.
„ sulphuric acid „ = 1·11618.

These solutions contain 117·2 grams of magnesium sulphate and 183·2 grams of sulphuric acid per litre respectively:

Equimolecular volumes: $100MgSO_4,Aq$: $52·1H_2SO_4,Aq$.

I.	II.	I.	II
6·58	0·086	156·65	0·642
13·25	0·169	203·31	0·678
17·20	0·207	371·07	0·741
26·44	0·291	508·92	0·762
52·08	0·442	1116·50	0·797
104·68	0·578		

(V.) Mixtures of zinc sulphate with sulphuric acid.

Density of zinc sulphate solution = 1·16134.
„ sulphuric acid „ = 1·11631.

These solutions contain 166·3 grams of zinc sulphate and 183·2 grams of sulphuric acid per litre respectively:

Equimolecular volumes : $100ZnSO_4,Aq : 55·6H_2SO_4,Aq$.

I.	II.	I.	II.
7·21	0·067	110·59	0·435
14·00	0·129	166·07	0·501
18·29	0·158	221·77	0·544
27·51	0·215	444·26	0·568
55·62	0·330		

(VI.) Mixtures of copper sulphate with sulphuric acid.

Density of copper sulphate solution = 1·15655.
„ sulphuric acid „ = 1·11896.

These solutions contain 158·0 grams of copper sulphate and 187·8 grams of sulphuric acid per litre respectively : $CuSO_4$ anhydrous

Equimolecular volumes : $100CuSO_4,Aq : 51·7H_2SO_4,Aq$.

I.	II.	I.	II.
6·57	0·055	103·06	0·348
12·75	0·095	154·80	0·397
17·59	0·121	207·37	0·412
25·91	0·170	409·75	0·456
51·82	0·259		

(VII.) Mixtures of aluminium sulphate with sulphuric acid.

Density of aluminium sulphate solution = 1·18833.
„ sulphuric acid „ = 1·15374.

These solutions contain 214·3 grams of aluminium sulphate and 246·3 grams of sulphuric acid per litre respectively :

Equimolecular volumes : $100Al_2 SO_4)_3,Aq : 24·9H_2SO_4,Aq$.

I.	II.	I.	II.
8·55	0·110	100·11	0·527
16·93	0·187	150·06	0·604
24·99	0·247	300·46	0·689
50·03	0·385		

The changes in volume occurring when these solutions are mixed together in the proportions requisite to yield 100 gram-molecules of the salt and acid were calculated as follows.

From the expansion curve of sodium sulphate and sulphuric acid mixtures, for instance, 100 volumes of Na_2SO_4,Aq, when mixed with 43·12 volumes of H_2SO_4,Aq, yield an expansion of 0·581 volume.

Since 100 volumes of Na_2SO_4,Aq contain 11·21 grams of sodium sulphate, it follows that 1 gram-molecule is contained in 1268 volumes, and the change in volume when 50 gram-molecules of sodium sulphate are mixed with 50 of sulphuric acid is therefore $0·581 \times 12·68 \times 50$, or 368 volumes.

In the same way, when these substances are mixed together in the molecular proportion $3Na_2SO_4 : H_2SO_4$, that is, when 75 per cent. of sodium sulphate molecules are present, the expansion is equivalent to $0{\cdot}274 \times 12{\cdot}68 \times 75$, or 261 volumes.

Percentage gram-molecules of salt.	Expansions occurring in aqueous mixtures containing 100 gram-molecules of sulphuric acid and								
	(I.)		(II.)	(III.)	(IV.)	(V.)	(VI.)	(VII.)	
	Potassium sulphate.							Aluminium sulphate.	
	(a.)	(b.)						(a.)	(b.)
	Observed.	Calculated from expression $\xi = a(100 - a)K$.	Sodium sulphate.	Ammonium sulphate.	Magnesium sulphate.	Zinc sulphate.	Copper sulphate.	$Al_2(SO_4)_3$.	$\frac{1}{2}Al_2(SO_4)_3$.
88·9	139	155	129	114	78	55	48	57	58
80·0	234	252	217	191	138	99	77	106	94
75·0	279	295	261	232	159	115	91	126	112
66·7	340	350	322	284	199	140	114	160	131
50·0	394	—	368	321	226	160	130	196	152
33·3	338	350	318	263	196	141	117	202	140
25·0	269	295	259	207	163	122	100	186	120
20·0	230	252	215	168	139	106	83	169	102
11·1	137	155	126	97	85	61	51	113	66

Now if in these mixtures contractive influences were entirely eliminated, the change in volume, assuming that no chemical action occurs, should accord with the expression:

$$\xi = a(100 - a)K.$$

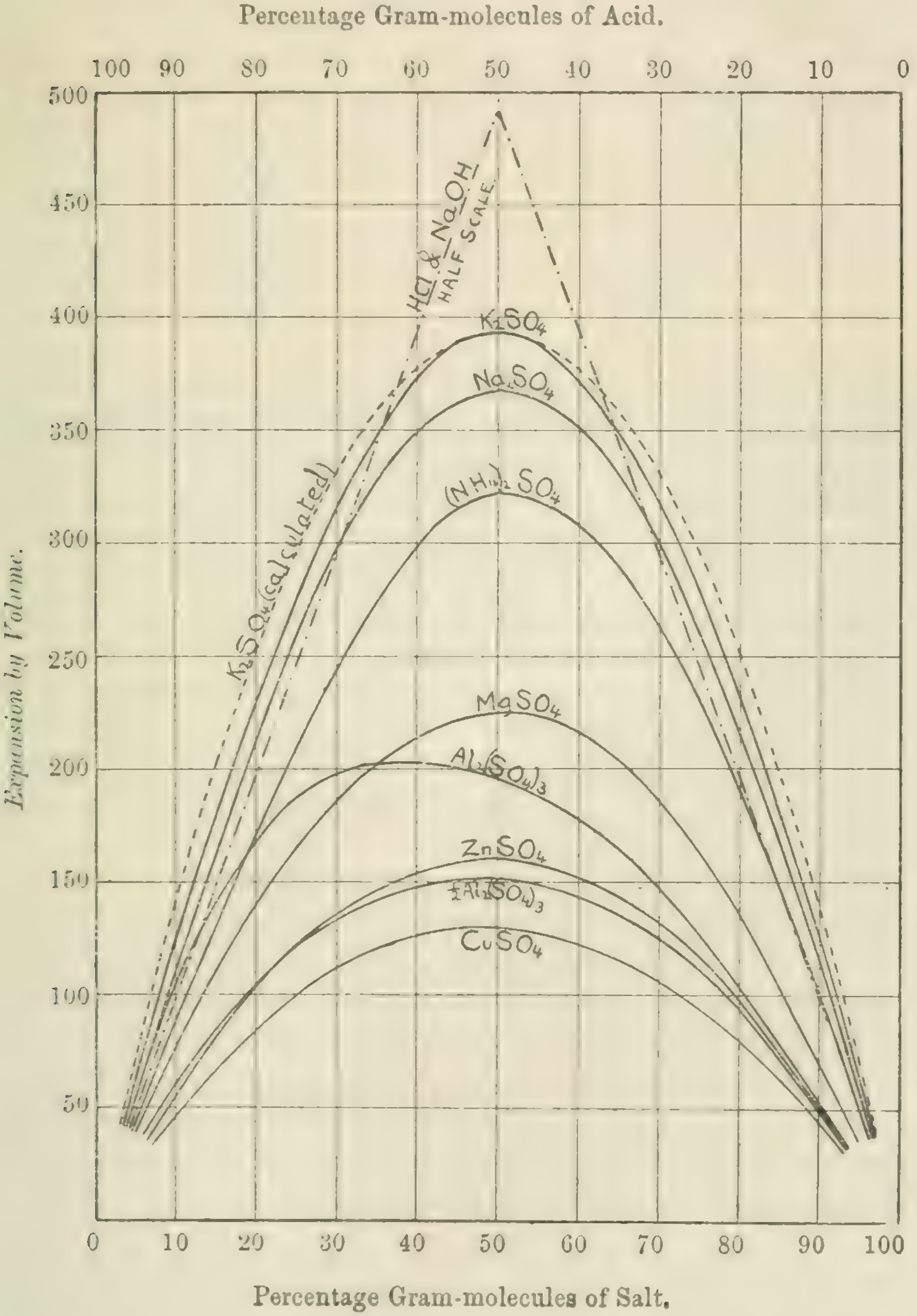
Calculating the value of K for aqueous potassium sulphate and sulphuric acid mixtures from the determined expansion at equimolecular mixtures, and substituting for other values of a, we get the figures in column (I*b*).

The comparison between the observed and calculated expansions is more clearly seen from the curves (Fig. 2).

It is evident that, in addition to the normal repulsion, there is a relatively small contractive force which has not been eliminated under the conditions of experiment. In the other mixtures, similar slight deviations from the theoretical are observed.

The general concordance of these curves, however, gives strong support to the view that the increases in volume are due to physical forces of repulsion between the molecules rather than to the formation of acid sulphates in solution.

FIG. 2.



Additional evidence is afforded by the change in volume attending mixtures of aqueous solutions of the neutral and acid sulphates of potassium, although there is here no question of chemical action.

Mixtures of Neutral Potassium Sulphate with Acid Potassium Sulphate Solutions.

Density of neutral potassium sulphate solution = 1·06898.
„ acid „ „ „ = 1·09104.

These solutions contain 88·7 grams of neutral sulphate and 134·7 grams of acid sulphate per litre respectively:

Volume of neutral potassium sulphate solution mixed with 100 volumes of the acid potassium sulphate solution.	Expansion in volume.
16·55	0·027
33·40	0·055
48·59	0·074
98·16	0·116
197·41	0·163
295·40	0·183
581·48	0·227

It is doubtful whether the acid sulphate molecule exists in aqueous solution. Berthelot (*Compt. rend.*, 1872, **75**, 207) proved from thermochemical considerations that both free sulphuric acid and neutral sulphate exist in aqueous solutions of acid potassium sulphate, and, more recently, Colson (*Compt. rend.*, 1903, **136**, 366) has shown that an aqueous solution of this salt behaves as a freshly prepared solution of the neutral sulphate and sulphuric acid, and on slow cooling deposits crystals of the neutral sulphate.

A determination of the free acid in solutions of a sample of Kahlbaum's pure acid sulphate of potassium at different concentrations proved that the molecule, if existent, is wholly dissociated in aqueous solution into equivalent quantities of the neutral salt and sulphuric acid.

In these circumstances, the above changes in volume should compare with those obtained in mixtures of the neutral sulphate with sulphuric acid. Thus, from the above data, we find that 1967 volumes of K_2SO_4,Aq contain 1 gram-molecule of the salt, whilst 2023 volumes of $KHSO_4$,Aq should now contain a gram-molecule each of the neutral salt and sulphuric acid. A mixture of the solutions therefore in these proportions by volume will represent the molecular mixture $2K_2SO_4,H_2SO_4$, and similarly for other molecular mixtures. The following figures were obtained by interpolation:

I. Molecular mixture.	II. Expansion by volume.	III. Expansion by volume in mixtures of 100 gram-molecules of potassium sulphate and sulphuric acid.
$2K_2SO_4,H_2SO_4$	$x+2·33$	340
$3K_2SO_4,H_2SO_4$	$x+3·18$	276
$4K_2SO_4,H_2SO_4$	$x+3·72$	232
$8K_2SO_4,H_2SO_4$	$x+4·67$	139

In Column II, x represents the expansion by volume appertaining to the molecular mixture K_2SO_4,H_2SO_4, and by substituting for x the value determined for it above, namely, $2 \times 3{\cdot}94$, we are enabled to calculate the expansions yielded at the different concentrations in mixtures of 100 gram-molecules (Column III). These are identical with the values obtained for aqueous potassium sulphate and sulphuric acid mixtures (p. 1614).

Further evidence in support of this theory is afforded when we consider the nature of the volumetric changes in aqueous mixtures, in which these changes can be referred almost exclusively to chemical forces.

The change in volume, being in these circumstances a rectilinear function of the intensity of chemical affinity, should accord with the expression :

$$\xi = \beta.\mathrm{K},$$

where ξ is the change in volume and β the number of molecules which have combined chemically.

The following results were obtained by mixing normal solutions of hydrochloric acid and sodium hydroxide :

Volume of *N*-sodium hydroxide mixed with 100 volumes of *N*-hydrochloric acid.	Expansion in volume.
12·59	0·251
25·17	0·495
33·51	0·657
49·63	0·976
100·57	1·978
202·10	1·934
299·74	1·916
402·66	1·887
803·50	1·862

Calculating as before from the expansion curves, the following figures are obtained for mixtures of 100 gram-molecules of alkali and acid :

I. Number of gram-molecules of hydrochloric acid in the initial volumes.	II. Number of molecules which have combined chemically.	III. Expansion.	
		(*a.*) Observed.	(*b.*) Calculated from the expression : $\xi = \beta.K$.
88·9	22·2	223	218
80·0	40·0	395	394
75·0	50·0	490	492
66·7	66·7	653	656
50·0	100·0	984	—
33·3	66·7	644	656
25·0	50·0	479	492
20·0	40·0	377	394
11·1	22·2	207	218

When these expansions are plotted similarly to those obtained in the case of aqueous mixtures of sulphuric acid with its neutral salts (Fig. 2), the difference between chemical and physical forces in solution is more clearly seen.

It would appear from these considerations that the volumetric changes obtained when sulphuric acid and its neutral salts are mixed together in aqueous solution result from the action of physical forces inherent to the molecules, and are independent of chemical affinity (so-called) and the formation of acid sulphates. It follows, therefore, that in such mixtures the relative complexities of the interacting molecules can be deduced from a comparison of the volumetric changes at corresponding molecular mixtures and the weights of the bodies which yield a maximum deviation from the theoretical.

It is apparent from a consideration of the molecular expansion curves in the case of mixtures of sulphuric acid with the sulphates of potassium, sodium, ammonium, magnesium, zinc, and copper, that these substances are similarly aggregated in solution. In the case of aluminium sulphate, however, on the assumption that its molecule can be represented by $Al_2(SO_4)_3$, as compared with H_2SO_4 for the molecule of sulphuric acid, the expansions at corresponding concentrations are not comparable, and the maximum occurs at the molecular mixture $Al_2(SO_4)_3,2H_2SO_4$. The molecule of sulphuric acid must therefore be represented by $(H_2SO_4)_2$ if that of aluminium sulphate is $Al_2(SO_4)_3$, and confirmation of this is afforded when the changes in volume are calculated according to this view (Column VII*b*).

Many additional mixtures were made with a view to eliminating the slight differences between the observed and calculated expansion curves. From the fact, however, that the contraction curves of water with the several constituents of the mixtures were not quite of the same order, this could not be done. For, although these curves could be superimposed through a considerable range without fear of the slight differences leading to discrepancies in the determination of the relative aggregations of the interacting substances, the differences between the curves increased with the distance from the point of coincidence. When attempts were made to obviate this by mixing together, at these extreme concentrations, solutions which yielded exactly the same contraction, it was found that the increased differences in the densities of the two solutions caused a still greater deviation from the theoretical, probably due to the gravitating effect of differences in mass already advanced in the case of mixtures of pure liquids. Conversely by mixing solutions containing equal proportions by weight of the interacting substances, the divergence of the two curves became more accentuated, proving that in these mixtures complete elimination of extraneous influences could not be effected.

So long, however, as the mixtures with water gave contraction curves of approximately equal slope, according to the method given above for the elimination of disturbing influences around the point of equimolecular mixtures, the molecular expansion curves obtained were practically identical at varying dilutions, proving that no breaking down of molecular complexes occurs on dilution, but that within a very considerable range each molecule retains its individuality.

It will be noticed that the method of interpreting volumetric changes here employed in cases of substances which mix together without apparent molecular change is antagonistic to the existence of hydrates in solutions of inorganic salts, just as has been already demonstrated in the case of organic solutions (*loc. cit.*). The neutral anhydrous sulphates of potassium and ammonium, for instance, give with sulphuric acid a maximum expansion at the same molecular mixtures as the variably hydrated sulphates of copper, sodium, &c., whereas if the latter consisted of molecular complexes containing water chemically combined, these results would not be expected. On similar grounds, it is probable that the molecules of acid sulphates have no individual existence in aqueous solutions, but appear as mixtures of the neutral salt and sulphuric acid in molecular proportions, and this applies also to crystalline hydrated and double salts which are dependent on temperature and concentration for their composition and crystalline form.

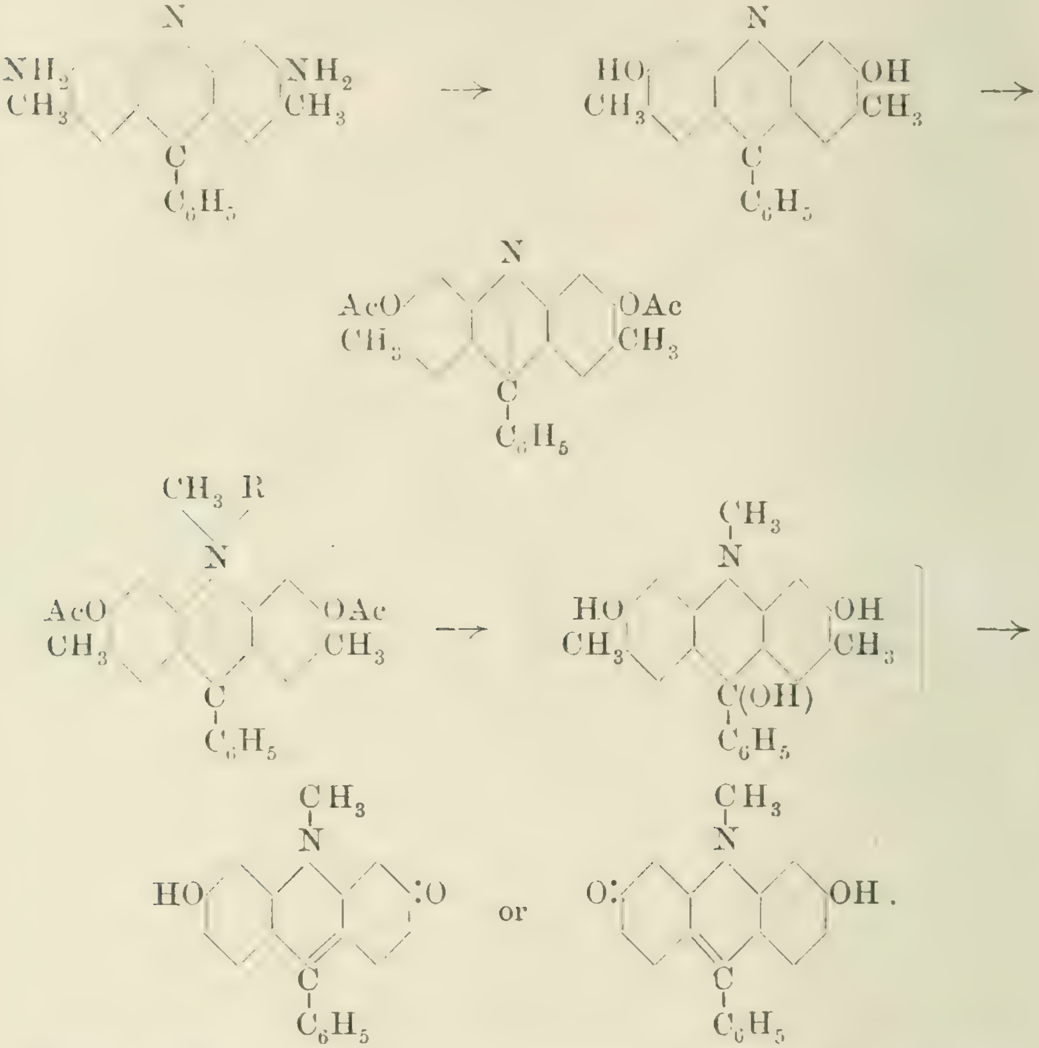
In conclusion, we wish to express our indebtedness to Dr. Thorpe, C.B., F.R.S., for facilities afforded us in carrying on this investigation.

GOVERNMENT LABORATORY.

CLIV.—*Benzoflavol* (2 : 8-*Dihydroxy*-5-*phenyl*-3 : 7-*dimethylacridine*).

By ALBERT ERNEST DUNSTAN and LOUISA CLEAVERLEY.

SINCE the displacement of amino-groups in positions 2 : 8 of the acridine nucleus by hydroxyl under the influence of acids at high temperature and under pressure is of a general nature (Cassella and Co., D.R.-P. 121686; Ullmann and Fitzenkam, *Ber.*, 1905, **38**, 3794; Dunstan and Hewitt, Trans., 1906, **89**, 1472), it seemed to us of interest to attempt a similar cycle of changes with benzoflavine as with chrysaniline in the hope of preparing an acridine base with hydroxyl groups in both or one of the 2 : 8-positions, presumably in both, considering the very symmetrical structure of the parent substance. This *dihydroxyacridine* has been prepared and successively acetylated, methylated, hydrolysed, and treated with alkali in accordance with the following scheme:



The benzoflavine used in this investigation was kindly obtained for us by Dr. Cain, to whom the authors take this opportunity of acknowledging their indebtedness.

This dyestuff is always loaded with dextrin, and the purification is apt to be troublesome in consequence. It was found that the best methods of purification were either to shake with dilute sulphuric acid, when the sparingly soluble sulphate of benzoflavine is formed, or to crystallise the acetate of the base from dilute acetic acid. In either case, the pure base was obtained by precipitation of its salts with alkali:

0·1812 benzoflavine gave 22 c.c. dry nitrogen at 25° and 754 mm.
N = 14·08.

$C_{21}H_{19}N_3$ requires N = 13·43 per cent.

The purified benzoflavine was heated in sealed tubes to 180°, during two days, with 30 per cent. sulphuric acid. In the initial experiments, fuming hydrochloric acid was used, but the preparation proceeds more smoothly with sulphuric acid, and better yields are obtained.

On cooling and opening, the tubes were frequently almost filled with very dark red needles, quite homogeneous, and showing a green reflex:

0·1432 gave 4·2 c.c. dry nitrogen at 20° and 758 mm. N = 3·41.
0·3345 ,, 0·1316 H_2O and 9·9 c.c. dry nitrogen at 20° and 758 mm.
H = 4·37 ; N = 3·46.
0·3134 gave 0·1705 $BaSO_4$. S = 7·45.
$C_{21}H_{17}O_2N,H_2SO_4$ requires H = 4·60 ; N = 3·39 ; S = 7·74 per cent.[*]

The substance was therefore 2 : 8-*dihydroxy*-5-*phenyl*-3 : 7-*dimethylacridine sulphate* (*benzoflavol sulphate*). It can be crystallised unchanged from glacial acetic acid. The crystals, after being dried in a vacuum over lime, gave the following results on analysis:

0·1768 gave 5·6 dry nitrogen at 25° and 757 mm. and 0·0677 H_2O.
N = 3·65 ; H = 4·44 per cent.

Benzoflavol sulphate is sparingly soluble in water, but dissolves very readily in glacial acetic acid, exhibiting a dark green fluorescence. When the acid solution is poured into water, immediate hydrolysis takes place, and the free *base* is precipitated in a fairly pure condition. Apparently the majority of the salts of benzoflavol are similarly hydrolysed. Benzoflavine salts are much more stable, and hence the traces of benzoflavine which remain unchanged in the tube can be separated from the benzoflavol.

The base, purified by pouring the solution of its sulphate in acetic acid into ammonia, crystallised from alcohol in dark brown needles melting between 255° and 260°:

0·1675 gave 5·7 c.c. nitrogen at 17° and 763 mm. N = 4·01.

$C_{21}H_{17}O_2N$ requires N = 4·44 per cent.

Benzoflavol is very soluble in concentrated sulphuric acid with strong bluish-green fluorescence. On moderate dilution and addition of ferric chloride and potassium dichromate respectively, yellow precipitates are formed. In hydrochloric acid solution, it appears reddish-yellow; it is insoluble in ether, slightly soluble in toluene, but readily so in alcohol, giving a magnificent green fluorescence. The fluorescence is inhibited by dilute hydrochloric, sulphuric, or other acids.

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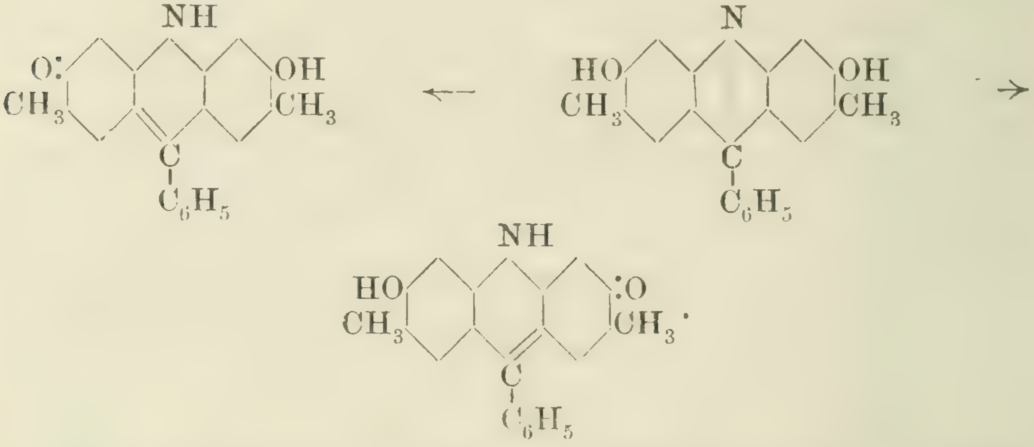
[*] The majority of the analyses in this paper were made by the method described recently by Young and Caudwell (*J. Soc. Chem. Ind.*, 1907, **26**, 184) with the introduction of a calcium chloride absorption tube between the furnace and the nitrometer. Young's generator for carbon dioxide supplies gas which is remarkably dry, and the only precaution to be taken is to avoid rushing the hot gas over the absorption apparatus in the preliminary clearing of the tube. Notwithstanding this, the percentage of hydrogen is frequently too low. The method is exceedingly convenient, and the apparatus deserves a place in every organic laboratory.

Potassium iodide precipitates yellow flocks from an acetic acid solution; nitric acid gives a dark red solution, whilst bromine water added to an acetic acid solution of benzoflavol furnishes a yellow precipitate.*

The scheme of symmetrical tautomeric link oscillation proceeding in the benzoflavol molecule is shown below:



It was found that chrysophenol was without fluorescence, owing to the asymmetry of the molecular vibration, and the order of increasing fluorescence is chrysophenol, chrysaniline, benzoflavol, benzoflavine, that is, in the order of increasing symmetry.

Benzoflavol Dichromate.—A solution of benzoflavol in acetic acid was slowly added to aqueous potassium dichromate. The resulting bright yellow, flocculent precipitate was collected, washed with hot water and alcohol, and dried at 110°. It does not melt below 250°:

0·0164 gave 0·0301 Cr_2O_3. Cr = 12·6.

$(C_{21}H_{17}O_2N_2)_2,H_2Cr_2O_7$ requires Cr = 12·3 per cent.

Benzoflavol Platinichloride.—This compound was prepared in the usual way from solutions of platinic chloride and the base in alcoholic hydrochloric acid. A red, crystalline substance separated, which did not melt below 275°.

On analysis of two distinct preparations, concordant results were obtained which pointed to the platinichloride either being very considerably hydrolysed or to its having a somewhat abnormal composition:

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* The action of the halogens generally on chrysaniline, benzoflavine, etc., is being at present studied in this laboratory.

0·1775 gave 0·0198 Pt. Pt = 11·2.
0·0691 „ 0·0079 Pt. Pt = 11·4.
$(C_{21}H_{17}O_2N)_4,H_2PtCl_6$ requires Pt = 11·6 per cent.

Benzoflavol Picrate.—This derivative was prepared by mixing alcoholic solutions of picric acid and the base, when an immediate precipitate was obtained which was dissolved by warming the liquid. On cooling, chocolate-brown needles separated, which were collected, washed with cold alcohol, and dried. They did not melt below 270°:

0·1293 gave 0·0468 H_2O and 11·2 c.c. dry nitrogen at 24° and 757 mm. H = 4·02; N = 10·0.
$C_{21}H_{17}O_2N,C_6H_3O_7N_3$ requires H = 3·68; N = 10·26 per cent.

Acetylation of Benzoflavol.—The base, purified as described above, was intimately mixed with twice its weight of fused sodium acetate and heated during four hours with five parts by weight of acetic anhydride. In this time, the originally dark orange-red colour gradually assumed a paler shade, as in the cases of benzoflavine, chrysaniline, and chrysophenol. After filtering from a dark tarry residue, ammonia was added to the filtrate in order to precipitate the orange-yellow *diacetylbenzoflavol.* It was purified by crystallisation from absolute alcohol, when it melted between 239—242°. For analysis, the substance was washed with alcohol and dried at 110°:

0·0244 gave 8 c.c. dry nitrogen at 27° and 750 mm. N = 3·78.
0·01468 „ 5·2 c.c. „ „ 18° „ 757 mm. N = 4·16.
$C_{25}H_{21}O_4N$ requires N = 3·51 per cent.

In acetic acid solution, the acetyl derivative gives the bright bluish-green fluorescence characteristic of the acridine nucleus.

Diacetylbenzoflavol is insoluble in alkalis, but is slightly soluble in water, and its very dilute aqueous solution shows distinct fluorescence. In alcohol, it gives a magnificently fluorescent solution, the fluorescence of which is much diminished on addition of hydrochloric acid. Bromine water precipitates a yellow, amorphous substance from the alcoholic solution of the acetyl derivative. Cold concentrated sulphuric acid dissolves it, giving a characteristic bluish-green fluorescence, which disappears on warming or on dilution.

The tarry residue mentioned above was dissolved in acetic acid and poured into potassium dichromate solution, when it yielded a yellowish-brown precipitate which was washed with water and alcohol and dried at 110°. It did not melt below 250°. Analysis showed it to be *diacetylbenzoflavol dichromate*:

0·0976 gave 0·0139 Cr_2O_3. Cr = 9·94.
$(C_{25}H_{21}O_4N)_2,H_2Cr_2O_7$ requires Cr = 10·2 per cent.

The *platinichloride* was made by adding excess of platinic chloride to a solution of diacetylbenzoflavol in alcoholic hydrochloric acid. The precipitate was redissolved by warming, and, when cold, deposited crystalline flakes which, after drying at 110°, were analysed:

0·2247 gave 0·0211 Pt. Pt = 9·39.
0·0433 „ 0·0041 Pt. Pt = 9·49.
$(C_{25}H_{21}O_4N)_4,H_2PtCl_6$ requires Pt = 9·77 per cent.

Benzoylation of Benzoflavol.—On benzoylating benzoflavol in sodium hydroxide solution, according to the Schotten-Baumann method, a gummy product was obtained. The alcoholic solution, however, on being poured into water, yielded a yellow, flocculent precipitate, which after being washed with a little alcohol was dried in a vacuum. Analysis showed that this was *dibenzoylbenzoflavol*:

0·1562 gave 4·7 c.c. dry nitrogen at 27° and 771 mm. and 0·0586 H_2O. N = 3·39; H = 4·17.
$C_{35}H_{25}O_4N$ requires N = 2·68; H = 4·77 per cent.

Dibenzoylbenzoflavol Chromate.—This substance was prepared by adding an alcoholic solution of the benzoyl derivative to aqueous potassium chromate. It separated as a brown precipitate, which was washed with alcohol and dried at 110°:

0·0982 gave 0·0112 Cr_2O_3. Cr = 7·61.
$(C_{35}H_{25}O_4N)_2,H_2Cr_2O_7$ requires Cr = 8·2 per cent.

Methylation of Diacetylbenzoflavol.—The methylation was accomplished in two ways, namely, by means of dimethyl sulphate and methyl iodide. In the first case, the acetyl derivative, mixed with considerable excess of dimethyl sulphate, was heated to boiling point for half an hour. The initial dark green fluorescence soon disappeared and was succeeded by a deep red colour. The product was dissolved in hot water and hydrolysed by boiling for a hour with 30 per cent. sulphuric acid. On cooling, a mass of brown crystals separated. The mother liquors showed only faint fluorescence, owing to the inhibition of link oscillation by the methyl group. The *sulphate* of the *anhydro-base* was washed with alcohol and dried at 110°:

0·1090 gave 0·0555 $BaSO_4$. S = 6·99.
$C_{22}H_{19}O_2N,H_2SO_4$ requires S = 7·49 per cent.

On adding ammonia to a solution of this sulphate, a brown precipitate resulted, which darkened considerably on being dried. It was not found possible to obtain it in a crystalline condition, so it was repeatedly extracted with boiling water, washed with alcohol, and dried at 110°:

0·0674 gave 0·0399 H_2O and 1·1976 CO_2. H = 6·5; C = 79·9.
0·1091 ,, 4·5 c.c. dry nitrogen at 27° and 756 mm. N = 4·74.
$C_{22}H_{19}O_2N$ requires H = 5·78; C = 80·2; N = 4·26 per cent.

This *anhydro-base* is exceedingly hard to burn, and the combustions were necessarily protracted, which accounts for the high numbers found for nitrogen and hydrogen. It is soluble in alcohol to a faintly fluorescent solution, and it dissolves in acids giving a deep red colour. From its solution in hydrochloric acid, a *platinichloride* and a *chromate* were prepared. The same abnormality which was noticed in the case of the platinichloride of benzoflavol and its diacetyl derivative was observed again in this case. The *platinichloride* of the base was a brown, amorphous substance. It was washed with alcohol and dried at 110°:

0·1519 gave 0·0174 Pt. Pt = 11·4.
$(C_{22}H_{19}O_2N)_4,H_2PtCl_6$ requires Pt = 11·3 per cent.

The methylation of diacetylbenzoflavol was also carried out by heating it with a slight excess of methyl iodide dissolved in five parts by weight of methyl alcohol to 130° during four hours. On cooling, the crystalline contents of the tube were recrystallised from methyl alcohol, when garnet-red needles with a fine green reflex separated. For analysis, the substance was dried at 110°. The Carius method entirely failed to give concordant results, owing to the formation of a double acridine silver nitrate. The Piria-Schiff method, modified by the addition of a little sodium peroxide, furnished more satisfactory numbers:

0·0960 gave 0·0424 AgI. I = 23·9.
$C_{26}H_{25}O_4NI$ requires I = 23·4 per cent.

Diacetylbenzoflavol methiodide, after precipitation with alkali and hydrolysis, gave the same anhydro-base as before. This was characterised by its *chromate*:

0·1678 gave 0·0175 Cr_2O_3. Cr = 7·13.
$(C_{22}H_{19}O_2N)_2,H_2CrO_4$ requires Cr = 6·70 per cent.

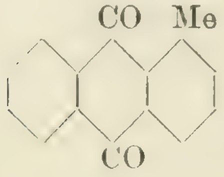
The authors desire to thank Dr. Hewitt for his interest in this work.

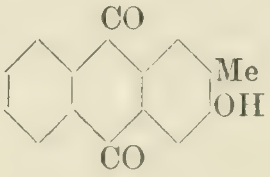
EAST HAM TECHNICAL COLLEGE.

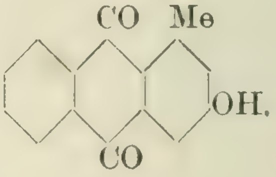
CLV.—*Researches on Anthraquinones and Phthaleins.*

By William Henry Bentley, Henry Dent Gardner, jun., and
Charles Weizmann.

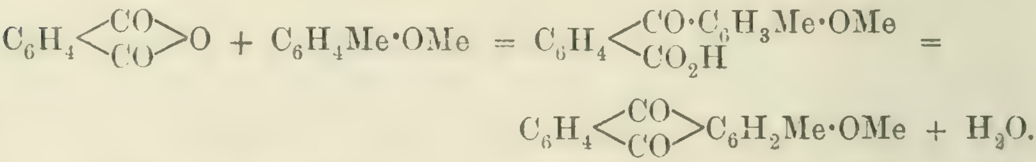
Of the fourteen possible hydroxymethylanthraquinones, only three are known with any degree of certainty, namely, the 4 : 1-, 3 : 2-, and 3 : 1-derivatives, which have been prepared from *p*-, *o*-, and *m*-cresol respectively:


4 : 1.


3 : 2.


3 : 1.

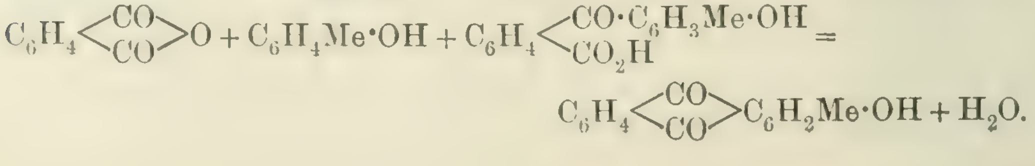
In addition, another has been described by Römer and Link (*Ber.*, 1883, **16**, 700), who obtained it from amino-2-methylanthraquinone, but were unable to determine its constitution. As the subject possessed considerable interest for us, we determined to prepare derivatives of this series by the action of aluminium chloride on a mixture of phthalic anhydride and the cresol methyl ethers, a reaction resulting in the formation of derivatives of benzoylbenzoic acid, which when heated with concentrated sulphuric acid condense to derivatives of anthraquinone:



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + C_6H_4Me\cdot OMe = C_6H_4<\begin{matrix}CO\cdot C_6H_3Me\cdot OMe\\CO_2H\end{matrix} = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Me\cdot OMe + H_2O.$$

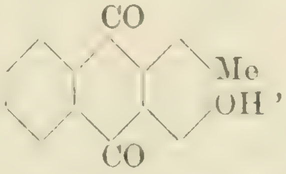
This reaction was employed by Nourrisson (*Ber.*, 1886, **19**, 2103) for the preparation of *p*-methoxybenzoylbenzoic acid and of 2-methoxyanthraquinone from phthalic anhydride and anisole.

In the condensation with sulphuric acid to the quinone, it was usually found that a certain amount of the methoxy-compound had suffered hydrolysis, so that hydroxymethylanthraquinone was also obtained. At the same time, we discovered that phthalic acid could be directly condensed with the cresols by means of boric acid, and in this way hydroxymethylbenzoylbenzoic acids were prepared, which on further treatment with sulphuric acid yielded hydroxymethylanthraquinone:

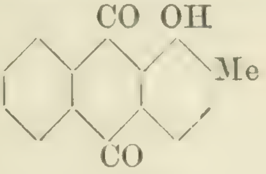


$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + C_6H_4Me\cdot OH + C_6H_4<\begin{matrix}CO\cdot C_6H_3Me\cdot OH\\CO_2H\end{matrix} = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Me\cdot OH + H_2O.$$

It is quite apparent that from *p*-cresol, only one hydroxymethylanthraquinone could result from either method of condensation, and such proved to be the case, but the products from *o*- and *m*-cresol were much more interesting, inasmuch as they differed according to the method of preparation. Thus, when *o*-cresol is condensed with boric acid, the hydroxymethylanthraquinone finally obtained melted at 185—186°, whereas the product furnished by the aluminium chloride method melted above 300°, neither of them being identical with that prepared by Fraude (*Annalen*, 1880, **202**, 165) from *o*-cresol, namely,

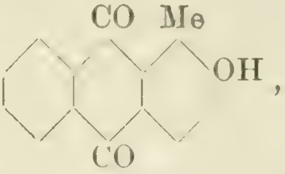


which melts at 260—262°. The possible formulæ for our two new hydroxymethylanthraquinones are therefore:



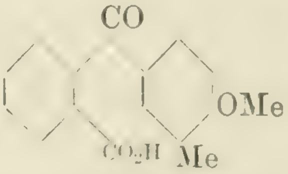
(I.)

and

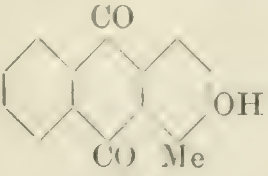


(II.)

and we venture to assign the first formula to the product obtained from the boric acid condensation and the second to that from the aluminium chloride condensation on the following grounds. When phthalic anhydride and anisole are condensed by means of aluminium chloride, the anisole is substituted in the para-position with regard to the methoxyl group, and as it can be fairly safely assumed that *o*-cresol methyl ether would act similarly to anisole the formula of the intermediate acid is

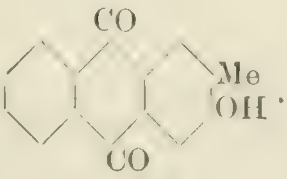


This acid, on further condensation and hydrolysis, can give rise to two different quinones, namely,



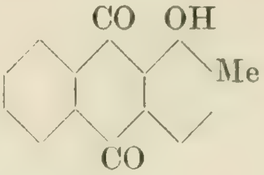
(I.)

and



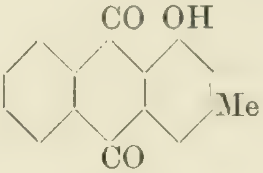
(II.)

The second is already known (Fraude, *loc. cit.*), so that the first is the formula of the hydroxymethylanthraquinone (m. p. above 300°) prepared by the aluminium chloride method. The remaining formula,



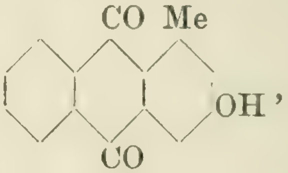
must therefore represent the hydroxymethylanthraquinone (m. p. 185—186°) from the boric acid condensation product. This would indicate that boric acid promotes condensation in the ortho-position with respect to the hydroxyl group, and this is well exemplified in the condensation of phthalic anhydride with *a*-naphthol in presence of boric acid, when substitution in the naphthol nucleus takes place almost exclusively in the ortho-position with respect to the hydroxyl group. Nevertheless, in the case of *o*-cresol, the production of some *o*-cresolphthalein shows that the para-position is also attacked.

As *m*-cresol can only give rise to two hydroxymethylanthraquinones,



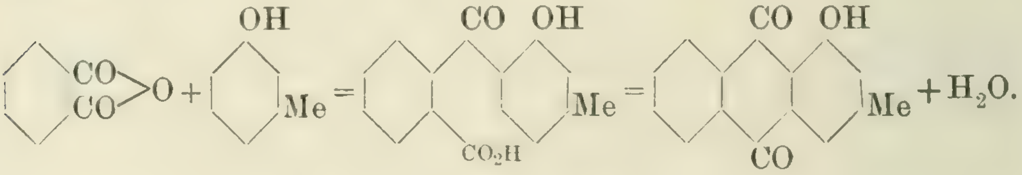
(I.)

and

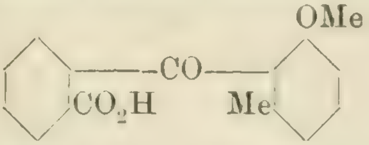


(II.)

the second of which is known and melts at 299—300° (Bistrzycki and Yssel de Schepper, *Ber.*, 1898, **31**, 2790), the products of our reaction should have been easily identified. This was so in the case of the boric acid condensation product, which behaved quite normally, yielding a hydroxymethylanthraquinone (m. p. 178°) which in all probability is identical with that prepared by Römer and Link (*Ber.*, 1883, **16**, 700) from amino-2-methylanthraquinone, who found practically the same melting point, namely, 177—178°. The reaction, in conformity with our rule that boric acid promotes the ortho-substitution, can be expressed thus:



The condensation with aluminium chloride, however, gave very confusing results. The intermediate acid melted at a very low temperature (61°), and when treated with concentrated sulphuric acid gave an exceedingly poor yield of methoxy- and hydroxy-methylanthraquinone, the latter having rather a low melting point (150°). In view of these facts, we are of the opinion that the intermediate acid consists mainly of 2′-methoxy-6′-methylbenzoylbenzoic acid,



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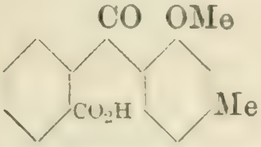
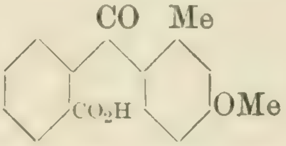
mixed with one or both of the other possible isomerides,



and



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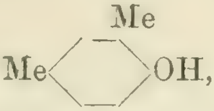
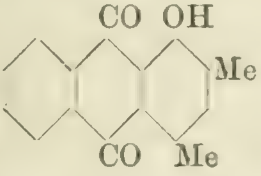
and that the hydroxymethylanthraquinone melting at 150° is a mixture.

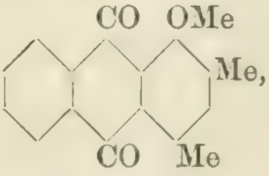
In addition to the cresols, *m*-4-xylenol and its methyl ether have been condensed with phthalic acid by the two methods at our disposal: hydroxydimethylanthraquinone being obtained in one case and methoxydimethylanthraquinone in the other. From a consideration of the formula of *m*-4-xylenol,



it is evident that the constitutions of these two quinones are



and



but we have not been able to prove that one is the methyl ether of the other, as we found it impossible to methylate the hydroxy-compound, and the methoxy-derivative is only hydrolysed by sulphuric acid with difficulty, this process also being attended with considerable decomposition.

In addition to the derivatives of benzoylbenzoic acid, there were usually obtained by the boric acid condensations the corresponding fluorans, which are characterised by their fluorescence in concentrated sulphuric acid solution.

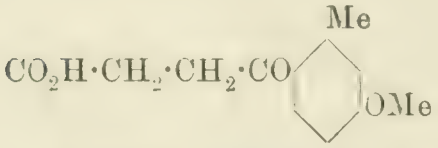
By means of boric acid, 4-hydroxyphthalic acid was also condensed with the cresols and *m*-4-xylenol. In the case of *o*-cresol, it was only possible to isolate the hydroxycresolphthalein, but from *m*- and *p*-cresols the corresponding benzoylbenzoic acids, the fluorans, and the anthraquinones were all prepared. Indeed, in the case of *m*-cresol, there was evidence that two series of these substances were to be obtained, although we were only successful in isolating one series in the pure state. The experiment with *m*-4-xylenol was interesting from the fact that the anthraquinone was obtained directly from the boric acid fusion and that no fluoran was found.

Several experiments were also conducted on the boric acid condensation of phthalic acid with other para-substituted phenols. Quinol and toluquinol did not yield the intermediate acids, but formed directly the corresponding quinizarin and methylquinizarin respectively.

Experiments with bromo-*o*-cresol and bromo-*p*-cresol resulted in the elimination of hydrogen bromide and the formation of dihydroxymethylanthraquinones, which, however, were not obtained sufficiently pure for analysis.

Diphenol and dinaphthol were also found to give condensation products, a description of which will be reserved for a future communication.

At the end of this paper, an account is given of some experiments on the condensation of succinic and maleic anhydrides on cresol methyl ether in presence of aluminium chloride. The acids prepared have probably the following constitutions:



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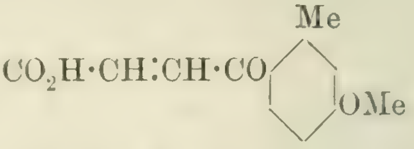

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but no success has yet attended our efforts to effect further condensation without decomposition.

EXPERIMENTAL.

Condensations with Aluminium Chloride.

4′-*Methoxy*-5′-*methyl*-2-*benzoylbenzoic acid*,*

$$CO_2H·C_6H_4·CO·C_6H_3Me·OMe.$$

—Aluminium chloride (240 grams) is added in three portions to a mixture of *o*-cresol methyl ether (200 grams) and phthalic anhydride (240 grams) in carbon disulphide, and the whole heated on the water-bath for ten to fifteen hours. After decanting the carbon disulphide, the hard product is treated with a large quantity of ice and hydrochloric acid, whereby the acid is obtained as an oily mass. Volatile impurities are removed by steam, and the residue is dissolved in sodium carbonate and reprecipitated with hydrochloric acid, being finally crystallised from methyl alcohol, from which it separates as a white powder melting at 176°:

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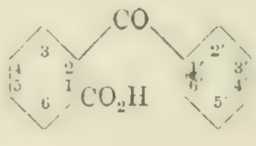
* Method of nomenclature:



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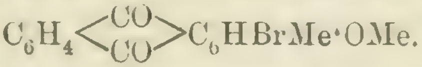
0·1418 gave 0·3680 CO_2 and 0·0653 H_2O. C = 70·77 ; H = 5·11.
$C_{16}H_{14}O_4$ requires C = 71·11 ; H = 5·18 per cent.

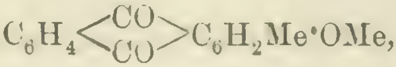
4′-Methoxy-5′-methyl-2-benzoylbenzoic acid is soluble in alcohol, acetic acid, ether, or benzene, but very sparingly so in hot water. When heated in glacial acetic acid with one molecular equivalent of bromine, it yields the *monobromo*-derivative, which is obtained as an oil on pouring the product in water ; it is dissolved in sodium carbonate, reprecipitated with acid, and crystallised from glacial acetic acid, from which it separates in yellow needles melting at 219—220° :

0·1230 gave 0·2666 CO_2 and 0·0450 H_2O. C = 55·08 ; H = 3·78.
0·1240 „ 0·3797 AgBr. Br = 22·8.
$C_{16}H_{13}O_4Br$ requires C = 55·01 ; H = 3·44 ; Br = 22·9 per cent.

Bromo-4-methoxy-5′-methyl-2-benzoylbenzoic acid is soluble in alcohol or acetic acid ; it dissolves in concentrated sulphuric acid forming a red solution, which becomes darker on heating, and a compound is produced which is probably *bromomethoxymethylanthraquinone*,

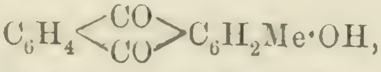

$$C_6H_4{<}\substack{CO\\CO}{>}C_6HBrMe{\cdot}OMe.$$

This crystallises from alcohol in greenish-yellow needles melting at 179—180°.

2-Methoxy-1-methylanthraquinone,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2Me{\cdot}OMe$, is produced when 4′-methoxy-5′-methyl-2-benzoylbenzoic acid is heated to 155° in concentrated sulphuric acid. The formation of the quinone is indicated by the solution becoming intensely red, and on pouring the product into cold water a yellow precipitate is obtained. This is collected, well washed with hot dilute potassium hydroxide to remove the hydrolysed quinone, and crystallised from methyl alcohol, from which it separates in canary-yellow needles melting at 184° and subliming somewhat readily :

0·1187 gave 0·3305 CO_2 and 0·0507 H_2O. C = 75·93 ; H = 4·74.
$C_{16}H_{12}O_3$ requires C = 76·19 ; H = 4·76 per cent.

2-Methoxy-1-methylanthraquinone is soluble in acetic acid or alcohol ; its solution in concentrated sulphuric acid is scarlet.

2-Hydroxy-1-methylanthraquinone,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2Me{\cdot}OH$, is precipitated when the alkaline liquors from the foregoing quinone are acidified. It crystallises from glacial acetic acid in yellow needles melting above 300° :

0·1293 gave 0·3565 CO_2 and 0·0493 H_2O. C = 75·19 ; H = 4·24.
$C_{15}H_{10}O_3$ requires C = 75·63 ; H = 4·20 per cent.

2-Hydroxy-1-methylanthraquinone dissolves in alcohol or benzene ;

its *potassium* salt is sparingly soluble in cold water with a reddish-violet colour.

Monobromo-2-methoxy-1-methylanthraquinone is prepared by heating a solution of 2-methoxy-1-methylanthraquinone in glacial acetic acid with one molecular proportion of bromine on the water-bath until the bromine has disappeared. The bromo-compound which separates out on cooling, crystallises from glacial acetic acid in yellow needles melting at 228°:

0·1027 gave 0·2178 CO_2 and 0·0303 H_2O. C = 57·83; H = 3·27.
0·1130 ,, 0·0643 AgBr. Br = 24·3.
$C_{16}H_{11}O_3Br$ requires C = 58·00; H = 3·32; Br = 24·1 per cent.

Bromo-2-methoxy-1-methylanthraquinone is sparingly soluble in alcohol, and dissolves in sulphuric acid with a red colour which on heating changes to brown.

Mononitro-2-methoxy-1-methylanthraquinone is formed when 2-methoxy-1-methylanthraquinone is dissolved in cold fuming nitric acid. The product is poured into water, the precipitate washed with water and afterwards with dilute potassium hydroxide, and crystallised with acetic acid, from which it separates in canary-yellow needles which melt at 179°:

0·1537 gave 6·2 c.c. nitrogen at 17° and 762 mm. N = 4·7.
$C_{16}H_{11}O_5N$ requires N = 4·7 per cent.

Mononitro-2-methoxy-1-methylanthraquinone dissolves in cold concentrated sulphuric acid forming an orange-red solution which becomes blood-red on heating. When treated with stannous chloride and potassium hydroxide, it is reduced to *amino-2-methoxy-1-methylanthraquinone*, which crystallises from methyl alcohol in bright red needles melting at 181°, and forms a *hydrochloride* which decomposes in water. On boiling with acetic anhydride, the amino-compound yields *acetylamino-2-methoxy-1-methylanthraquinone*, which crystallises from glacial acetic acid in brown needles melting at 204°:

0·1423 gave 0·3649 CO_2 and 0·0616 H_2O. C = 69·93; H = 4·79.
0·1870 gave 7·2 c.c nitrogen at 16° and 767 mm. N = 4·53.
$C_{18}H_{15}O_4N$ requires C = 69·92; H = 4·85; N = 4·53 per cent.

It forms a pale red solution with sulphuric acid.

Mononitro-2-hydroxy-1-methylanthraquinone.—This substance is also produced in the nitration of methoxymethylanthraquinone owing to hydrolysis of the methoxyl group, and is obtained from the alkaline wash water by precipitation with hydrochloric acid. It crystallises from acetic acid in pale yellow, feathery needles melting at 167—168°:

0·1358 gave 5·7 c.c. nitrogen at 18° and 764 mm. N = 4·85.
$C_{15}H_9O_5N$ requires N = 4·9 per cent.

Mononitro-2-hydroxy-1-methylanthraquinone dissolves in sulphuric acid with a carmine, and in alkalis with a brown, colour.

Trinitro-2-methoxy-1-methylanthraquinone is formed when an excess of fuming nitric acid is added to a solution of 2-methoxy-1-methylanthraquinone in sulphuric acid and the mixture allowed to stand for several hours. The product is isolated in the same manner as the mononitro-derivative. It separates from glacial acetic acid as a buff-coloured powder melting at 212° with decomposition :

0·2095 gave 19·2 c.c. nitrogen at 17° and 771 mm. $N = 10·8$.
$C_{16}H_9O_9N_3$ requires $N = 10·8$ per cent.

Trinitro-2-methoxy-1-methylanthraquinone is sparingly soluble in alcohol or cold sulphuric acid. In warm sulphuric acid it dissolves with a brown colour.

[With JOHN HAROLD ANDREW.]

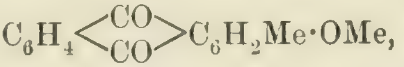
2′-Methoxy-5′-methyl-2-benzoylbenzoic acid,

$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OMe$,

is prepared from *p*-cresol methyl ether in the same manner as 4′-methoxy-5′-methyl-2-benzoylbenzoic acid from *o*-cresol methyl ether. It is soluble in alcohol, ether, or acetic acid, and sparingly so in water ; it melts at 122° :

Found, $C = 71·05$; $H = 5·11$.
$C_{16}H_{14}O_4$ requires $C = 71·11$; $H = 5·18$ per cent.

When heated to 150° with concentrated sulphuric acid, this acid condenses to

4-Methoxy-1-methylanthraquinone,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2Me\cdot OMe$, which is isolated and purified exactly like 2-methoxy-1-methylanthraquinone. It crystallises from methyl alcohol in orange-yellow needles which melt at 170—171° :

$C = 75·95$; $H = 4·91$.
$C_{16}H_{12}O_3$ requires $C = 76·19$; $H = 4·76$ per cent.

When strongly heated with concentrated sulphuric acid, hydrolysis occurs with the formation of 4-hydroxy-1-methylanthraquinone, which crystallises in yellow needles melting at 175° (Birukoff, *Ber.*, 1887, **20**, 2069, gives 179—170°) :

0·1492 gave 0·4134 CO_2 and 0·0583 H_2O. $C = 75·57$; $H = 4·33$.
$C_{15}H_{10}O_3$ requires $C = 75·63$; $H = 4·20$ per cent.

[With CLAUDE VAZEILLE TEMPERLEY.]

4(5): 2′-*Dimethoxy-5′-methyl-2-benzoylbenzoic acid*,

$OMe\cdot C_6H_3(CO_2H)\cdot CO\cdot C_6H_3Me\cdot OMe$.

—The acid is prepared from 4-methoxyphthalic anhydride and *p*-cresol methyl ether by the same process as used for 4′-methoxy-5′-methyl-2-benzoylbenzoic acid; it is best purified by repeated crystallisation from water, in which it is very sparingly soluble. It dissolves in alcohol, chloroform, or acetic acid, and melts at 157·5°:

0·1927 gave 0·4802 CO_2 and 0·0933 H_2O. C = 67·96; H = 5·38.

$C_{17}H_{16}O_5$ requires C = 68·00; H = 5·33 per cent.

When heated to 110° with concentrated sulphuric acid, it undergoes condensation and partial hydrolysis, yielding probably 6(7)-*hydroxy*-4-*methoxy*-1-*methylanthraquinone*, $HO\cdot C_6H_3<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>C_6H_2Me\cdot OMe$, which crystallises in yellow needles melting at 158°:

0·1176 gave 0·3070 CO_2 and 0·0490 H_2O. C = 71·19; H = 4·63.

$C_{16}H_{12}O_4$ requires C = 71·64; H = 4·48 per cent.

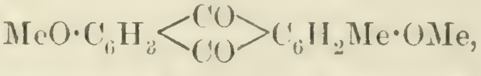
The presence of one methoxyl group was also confirmed by an estimation by Zeisel's method:

Found, OMe = 11·40.

$C_{15}H_9O_3\cdot OMe$ requires OMe = 11·55 per cent.

This quinone is readily soluble in alcohol, but only sparingly so in light petroleum or carbon disulphide. With potassium hydroxide it yields a deep red-coloured *potassium* salt.

4 : 6(7)-*Dimethoxy*-1-*methylanthraquinone*,



$$MeO\cdot C_6H_3<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>C_6H_2Me\cdot OMe,$$

is obtained by dissolving 4(5) : 2′-dimethoxy-5′-methyl-2-benzoylbenzoic acid together with a little boric acid in cold concentrated sulphuric acid and carefully adding fuming sulphuric acid (containing 60 per cent. of sulphur trioxide) so that the temperature does not rise above 40°. The product is poured into ice-water, the precipitate collected, washed, and crystallised from acetic acid. It melts at 141°, does not dissolve in dilute aqueous potassium hydroxide, and is distinguished from the foregoing quinone by its ready solubility in carbon disulphide.

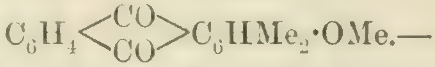
2′-*Methoxy*-3′ : 5′-*dimethyl-2-benzoylbenzoic acid*,

$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_2Me_2\cdot OMe$,

is prepared from *m*-4-xylenol methyl ether in the same way as 4′-methoxy-5′-methyl-2-benzoylbenzoic acid is prepared from *o*-cresol methyl ether. It melts at 188—189°:

0·1815 gave 0·4758 CO_2 and 0·0914 H_2O. C = 71·49 ; H = 5·58.
$C_{17}H_{16}O_4$ requires C = 71·83 ; H = 5·63 per cent.

2′-Methoxy-3′ : 5′-dimethyl-2-benzoylbenzoic acid is very soluble in alcohol or acetic acid, but only moderately so in benzene. It dissolves in cold sulphuric acid giving a dirty green solution, which on heating turns red owing to the formation of :

4-Methoxy-1 : 3-dimethylanthraquinone,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6HMe_2\cdot OMe$.—This quinone is isolated in the usual manner and, after crystallisation from acetic acid, melts at 176—177° :

0·1315 gave 0·3688 CO_2 and 0·0614 H_2O. C = 76·48 ; H = 5·19.
$C_{17}H_{14}O_3$ requires C = 76·69 ; H = 5·24 per cent.

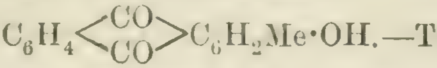
4-Methoxy-1 : 3-dimethylanthraquinone is soluble in acetic acid and sparingly so in alcohol or benzene. It is hydrolysed only with difficulty by sulphuric acid, and considerable decomposition ensues.

Condensations by Means of Boric Acid.

2′-Hydroxy-3′-methyl-2-benzoylbenzoic acid,
$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH$.
—This acid is prepared by heating a mixture of phthalic acid (or anhydride, 30 grams), *o*-cresol (30 grams), and boric acid (60 grams) to 170—180° until the yellow colour of the mixture commences to darken. The fusion is poured into a large quantity of water, boiled until free from *o*-cresol, and filtered hot. The residue consists of a mixture of *o*-cresolphthalein and hydroxymethylbenzoylbenzoic acid ; the latter is extracted by repeatedly boiling the residue with water and calcium carbonate, filtering, and acidifying the filtrates with hydrochloric acid. The precipitated acid is collected and crystallised from acetic acid, from which it separates in plates melting at 196—197° :

0·1265 gave 0·3260 CO_2 and 0·0563 H_2O. C = 70·28 ; H = 4·94.
$C_{15}H_{12}O_4$ requires C = 70·31 ; H = 4·68 per cent.

2′-Hydroxy-3′-methyl-2-benzoylbenzoic acid dissolves in alcohol, ether, or acetic acid, but is only sparingly soluble in hot water. It dissolves in cold concentrated sulphuric acid forming a yellow solution which turns orange-red on heating owing to the production of

1-Hydroxy-2-methylanthraquinone,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2Me\cdot OH$.—This substance is best prepared by dissolving the foregoing acid together with twice its weight of boric acid in concentrated sulphuric acid and carefully adding fuming sulphuric acid until the initial yellow colour changes to an intense red. The product is poured into water, the yellow precipitate filtered, washed with hot water, dried on porous porcelain, and crystallised from acetic acid, from which it separates in fibrous needles melting at 184—185°:

0·1942 gave 0·5374 CO_2 and 0·0752 H_2O. C = 75·47; H = 4·30.
$C_{15}H_{10}O_3$ requires C = 75·63; H = 4·20 per cent.

1-*Hydroxy-2-methylanthraquinone* dissolves in sulphuric acid with an orange-red colour. Its *potassium* salt is sparingly soluble in water, but readily so in alcohol with a bluish-red colour.

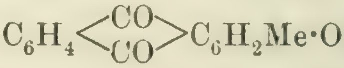
2′-*Hydroxy-4′-methyl-2-benzoylbenzoic acid*,

$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3Me{\cdot}OH$.

—This acid is prepared from *m*-cresol in the same manner as the corresponding acid from *o*-cresol. The dark red fusion is poured into water, boiled until free from *m*-cresol, and filtered. The residue, consisting of a mixture of the acid and the fluoran, is repeatedly extracted with boiling dilute aqueous sodium carbonate until no further precipitate appears on acidification. The united filtrates are acidified with hydrochloric acid, and the resulting white precipitate crystallised from methyl alcohol, from which it separates in prismatic plates melting at 210—211°:

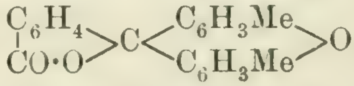
0·1382 gave 0·3560 CO_2 and 0·0603 H_2O. C = 70·25; H = 4·84.
$C_{15}H_{12}O_4$ requires C = 70·31; H = 4·68 per cent.

2′-*Hydroxy-4′-methyl-2-benzoylbenzoic acid* dissolves in sulphuric acid with a yellow colour, which changes to an intense orange-red on heating.

4-*Hydroxy-2-methylanthraquinone*,  $C_6H_4{<}{\scriptsize\begin{matrix}CO\\CO\end{matrix}}{>}C_6H_2Me{\cdot}OH$, is prepared from the foregoing acid and purified in the same manner as 1-hydroxy-2-methylanthraquinone:

0·1200 gave 0·3328 CO_2 and 0·0450 H_2O. C = 75·63; H = 4·16.
$C_{15}H_{10}O_3$ requires C = 75·63; H = 4·20 per cent.

This quinone melts at 178°, and is probably identical with that described by Römer and Link (*loc. cit.*). It is soluble in alcohol or acetic acid, from which it separates in yellow needles. Its *potassium* salt is sparingly soluble in water with a bluish-red colour.

3 : 6-*Dimethylfluoran*,[*]  $\begin{matrix}C_6H_4\\ |\\ CO{\cdot}O\end{matrix}{>}C{<}\begin{matrix}C_6H_3Me\\ C_6H_3Me\end{matrix}{>}O$.—This substance remains after the removal of the acid just described from the fused mixture of phthalic acid, boric acid, and *m*-cresol. It crystallises from acetic acid or xylene in short prisms melting at 204—205°:

0·1384 gave 0·4076 CO_2 and 0·0642 H_2O. C = 80·32; H = 5·15.
$C_{22}H_{16}O_3$ requires C = 80·48; H = 4·87 per cent.

3 : 6-*Dimethylfluoran* dissolves in concentrated sulphuric acid yielding a yellow, fluorescent solution.

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[*] For nomenclature, see Trans., 1902, **81**, 894.

2′-Hydroxy-5′-methyl-2-benzoylbenzoic acid,

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH,$$

is prepared from *p*-cresol and isolated from the fusion exactly like 2′-hydroxy-4′-methyl-2-benzoylbenzoic acid from *m*-cresol. It crystallises from methyl alcohol in plates melting at 194—195°:

0·1026 gave 0·2642 CO_2 and 0·0459 H_2O. C = 70·22; H = 4·97.
$C_{15}H_{12}O_4$ requires C = 70·31; H = 4·68 per cent.

2′-Hydroxy-5′-methyl-2-benzoylbenzoic acid dissolves in sulphuric acid, producing a yellow solution which, on the addition of boric acid and fuming sulphuric acid, changes to an orange-red owing to its condensation to 4-hydroxy-1-methylanthraquinone (p. 1633).

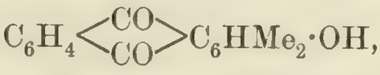
In the fusion of phthalic acid, boric acid, and *p*-cresol there is also formed 2 : 7-dimethylfluoran, which is isolated in the same way as the corresponding substance prepared from *m*-cresol. It melts at 250—252° (Drewsen, *Annalen*, 1882, **212**, 340, gives 246°) and dissolves in sulphuric acid forming a yellow solution more fluorescent than that produced by 3 : 6-dimethylfluoran.

2′-Hydroxy-3′ : 5′-dimethyl-2-benzoylbenzoic acid,

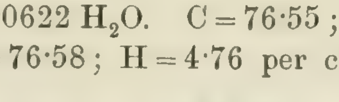
$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_2Me_2\cdot OH,$$

is produced by heating a mixture of phthalic acid, boric acid, and *m*-4-xylenol to 180° for two hours. The acid is isolated from the fusion exactly like 2′-hydroxy-4′-methyl-2-benzoylbenzoic acid. It crystallises from methyl alcohol in plates melting at 165—166°:

0·1256 gave 0·3284 CO_2 and 0·0590 H_2O. C = 71·31; H = 5·22.
$C_{16}H_{14}O_4$ requires C = 71·11; H = 5·18 per cent.

2′-Hydroxy-3′ : 5′-dimethyl-2-benzoylbenzoic acid dissolves in sulphuric acid with a yellow colour which changes to an orange-red on heating or on the addition of fuming sulphuric acid. On pouring the product into water, 4-*hydroxy*-1 : 3-*dimethylanthraquinone*,  $C_6H_4<\substack{CO\\CO}>C_6HMe_2\cdot OH$, is precipitated. It crystallises from acetic acid in prismatic needles melting at 173—175°:

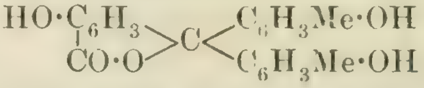
0·1420 gave 0·3986 CO_2 and 0·0622 H_2O. C = 76·55; H = 4·81.
$C_{16}H_{12}O_3$ requires C = 76·58; H = 4·76 per cent.

2 : 4 : 5 : 7-*Tetramethylfluoran*,  $\substack{C_6H_4\\|\\CO\cdot O}>C<\substack{C_6H_2Me_2\\C_6H_2Me_2}>O$.—This tetramethylfluoran is also a product of the fusion of phthalic acid, boric acid, and *m*-4-xylenol, and remains as a brown powder after the extraction with sodium carbonate. It is obtained pure by crystallising from xylene with the aid of animal charcoal, when it separates in prisms melting at 247—249°;

0·1126 gave 0·3344 CO_2 and 0·0584 H_2O. C = 80·99; H = 5·76.

$C_{24}H_{20}O_3$ requires C = 80·90; H = 5·62 per cent.

The solution of this substance in concentrated sulphuric acid possesses an orange colour, but little fluorescence.

Hydroxy-o-cresolphthalein, 
$\begin{array}{c}HO\cdot C_6H_3\\ |\\ CO\cdot O\end{array}>C<\begin{array}{c}C_6H_3Me\cdot OH\\ C_6H_3Me\cdot OH\end{array}$. —This substance was the only product which could be obtained from the fusion of 4-hydroxyphthalic acid, boric acid, and *o*-cresol by extraction with sodium carbonate. It crystallises from dilute acetic acid in white needles melting at 245—247°:

0·1290 gave 0·3435 CO_2 and 0·0577 H_2O. C = 72·62; H = 4·97.

$C_{22}H_{18}O_5$ requires C = 72·92; H = 4·94 per cent.

The substance dissolves in alkalis with a violet colour.

4(5) : 2′-*Dihydroxy*-4′-*methyl*-2-*benzoylbenzoic acid*,

$HO\cdot C_6H_3(CO_2H)\cdot CO\cdot C_6H_3Me\cdot OH$.

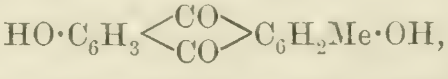
—This acid is prepared by heating a mixture of 4-hydroxyphthalic acid (30 grams), *m*-cresol (30 grams), and boric acid (60 grams) to 180° for two hours. The fused mass is poured into water, boiled, and filtered; the insoluble residue is then repeatedly boiled with water and calcium carbonate as long as the filtrate yields a precipitate on acidification. The united filtrates are acidified with hydrochloric acid, and the precipitate crystallised from acetic acid, from which it separates in plates melting at 228—229°:

0·1109 gave 0·2688 CO_2 and 0·0470 H_2O. C = 66·10; H = 4·70.

$C_{15}H_{12}O_5$ requires C = 66·17; H = 4·41 per cent.

4(5) : 2′-*Dihydroxy*-4′-*methyl*-2-*benzoylbenzoic acid* is sparingly soluble in water. It dissolves in concentrated sulphuric acid with an orange colour which changes to red on heating or treating with fuming sulphuric acid, due to its condensation to

4 : 7(8)-*Dihydroxy*-2-*methylanthraquinone*,



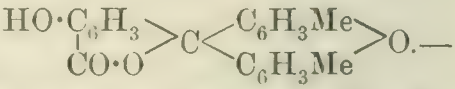
$$HO\cdot C_6H_3<\begin{array}{c}CO\\ CO\end{array}>C_6H_2Me\cdot OH,$$

which separates from acetic acid as a dull, yellow powder melting at 284°:

0·1088 gave 0·2818 CO_2 and 0·0398 H_2O. C = 70·64; H = 4·06.

$C_{15}H_{10}O_4$ requires C = 70·86; H = 3·93 per cent.

4 : 7(8)-*Dihydroxy*-2-*methylanthraquinone* is soluble in sodium carbonate or ammonia with an orange-red colour; it forms a dark red solution with sulphuric acid.

4′(5′)-*Hydroxy*-3 : 6-*dimethylfluoran*, 
$\begin{array}{c}HO\cdot C_6H_3\\ |\\ CO\cdot O\end{array}>C<\begin{array}{c}C_6H_3Me\\ C_6H_3Me\end{array}>O$.— This substance remains with the excess of calcium carbonate after the extraction of the last-mentioned acid, and is obtained by repeated

extraction with boiling sodium carbonate and acidification of the alkaline extract. The precipitate is collected and crystallised from dilute acetic acid, from which it separates in plates melting at 320—325°:

0·1196 gave 0·3346 CO_2 and 0·0524 H_2O. C = 76·30; H = 4·86.
$C_{22}H_{16}O_4$ requires C = 76·74; H = 4·65 per cent.

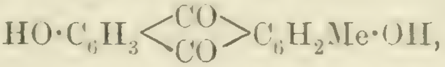
4′(5′)-*Hydroxy*-3 : 6-*dimethylfluoran* forms with sulphuric acid a yellow, but only slightly fluorescent, solution.

4(5) : 2′-*Dihydroxy-5′-methylbenzoylbenzoic acid*,

$HO\cdot C_6H_3(CO_2H)\cdot CO\cdot C_6H_3Me\cdot OH$.

—This acid is prepared from *p*-cresol in the same manner as the corresponding acid from *m*-cresol. It separates from methyl alcohol as a white powder melting at 234°. It dissolves in concentrated sulphuric acid with a yellow colour which on the addition of fuming sulphuric acid becomes dark red, indicating condensation to

4 : 6(7)-*Dihydroxy*-1-*methylanthraquinone*,



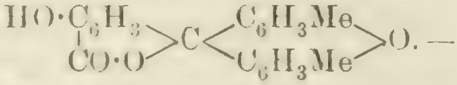
$HO\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2Me\cdot OH$,

which separates from alcohol or acetic acid as a yellow powder melting at 244—246°:

0·1162 gave 0·3002 CO_2 and 0·0422 H_2O. C = 70·46; H = 4·03.
$C_{15}H_{10}O_4$ requires C = 70·86; H = 3·93 per cent.

This compound dissolves in sodium carbonate and ammonia yielding orange-red solutions.

4′(5′)-*Hydroxy*-2 : 7-*dimethylfluoran*,



$\begin{matrix}HO\cdot C_6H_3\\ | \\ CO\cdot O\end{matrix}{>}C{<}\begin{matrix}C_6H_3Me\\ C_6H_3Me\end{matrix}{>}O$. —

This hydroxydimethylfluoran, prepared from *p*-cresol, is isolated and purified in the same way as the corresponding one from *m*-cresol. It crystallises in minute needles melting at 284°:

0·1134 gave 0·3186 CO_2 and 0·0472 H_2O. C = 76·62; H = 4·62.
$C_{22}H_{16}O_4$ requires C = 76·74; H = 4·65 per cent.

It dissolves in cold aqueous sodium hydroxide and in hot sodium carbonate. Its solution in concentrated sulphuric acid is yellow and fluorescent, but much less so than 2 : 7-dimethylfluoran.

4(5) : 2′-*Dihydroxy*-3′ : 5′-*dimethylbenzoylbenzoic acid*,

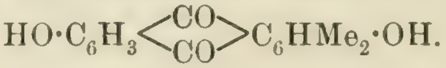
$HO\cdot C_6H_3(CO_2H)\cdot CO\cdot C_6H_2Me_2\cdot OH$.

—This acid is prepared from *m*-4-xylenol by the same process as that described for the corresponding acid from *m*-cresol. It crystallises from methyl alcohol in short prisms melting indefinitely at about 230°:

0·1303 gave 0·3203 CO_2 and 0·0578 H_2O. C = 67·04; H = 4·93.
$C_{16}H_{14}O_5$ requires C = 67·13; H = 4·89 per cent.

The compound dissolves in sulphuric acid with a yellow colour, which changes to a bluish-red on heating the solution.

4 : 6(7)-*Dihydroxy*-1 : 3-*dimethylanthraquinone*,



$$HO\cdot C_6H_3<\begin{matrix}CO\\CO\end{matrix}>C_6HMe_2\cdot OH.$$

—This quinone is prepared from the preceding acid in the usual way by treatment with fuming sulphuric acid. It was also found that the substance had been produced directly in the boric acid fusion, and was obtained in the sodium carbonate extract instead of the anticipated hydroxytetramethylfluoran. It crystallises from acetic acid in needles melting at 270° :

0·1395 gave 0·3668 CO_2 and 0·0590 H_2O. C = 71·71 ; H = 4·69.

$C_{16}H_{12}O_4$ requires C = 71·64 ; H = 4·48 per cent.

The compound dissolves in concentrated sulphuric acid with a bluish-red, and in sodium carbonate and ammonia with an orange-red, colour.

Methoxymethyl-β-benzoylpropionic acid,

$$MeO\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H.$$

—This acid is prepared by dissolving *m*-cresol methyl ether (30 grams) in a large quantity of carbon disulphide, adding succinic anhydride (25 grams) and aluminium chloride (10 grams), and heating the mixture on the water-bath in a reflux apparatus for six hours. The carbon disulphide is then decanted from the hard mass, which is disintegrated by the addition of ice and hydrochloric acid, and volatile impurities removed by steam. The residue is filtered, dissolved in sodium carbonate, precipitated with hydrochloric acid, and finally crystallised from water, from which it separates in colourless prisms melting at 131—132° :

0·1312 gave 0·3086 CO_2 and 0·0754 H_2O. C = 64·15 ; H = 6·38.

$C_{12}H_{14}O_4$ requires C = 64·86 ; H = 6·30 per cent.

Methoxymethyl-β-benzoylpropionic acid is soluble in alcohol, acetic acid or benzene. It yields a greenish-brown solution with concentrated sulphuric acid.

Methoxy-3-methyl-β-benzoylacrylic acid,

$$MeO\cdot C_6H_3Me\cdot CO\cdot CH\colon CH\cdot CO_2H.$$

—This acid is prepared from *o*-cresol methyl ether and maleic anhydride in exactly the same manner as the foregoing acid. It separates from benzene as a yellow powder melting at 113° :

0·1970 gave 0·4711 CO_2 and 0·0977 H_2O. C = 65·23 ; H = 5·51.

$C_{16}H_{12}O_4$ requires C = 65·45 ; H = 5·45 per cent.

The acid is very sparingly soluble in water, but readily so in alcohol, benzene, or acetic acid. It dissolves in sulphuric acid with a greenish-brown colour.

MANCHESTER UNIVERSITY.

CLVI.—*The Velocity and Mechanism of the Reaction between Iodine and Hypophosphorous Acid.*

By **Bertram Dillon Steele.**

When iodine and hypophosphorous acid are allowed to interact, the iodine slowly oxidises the hypophosphorous acid, the reaction proceeding with the formation of phosphorous or phosphoric acid according to the conditions of the experiment. Rupp and Finck (*Arch. Pharm.*, 1902, **240**, 663) propose for the estimation of phosphorous and hypophosphorous acids a method which is based on the fact that in acid solution the hypophosphorous acid is oxidised by iodine to phosphorous and not to phosphoric acid, whereas in the presence of an excess of sodium hydrogen carbonate, phosphorous acid is oxidised to phosphoric acid.

The foregoing statement implies that of the two reactions: (1) $H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$ and (2) $H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$, the former is catalytically accelerated by acids, whilst the latter is retarded.

Moreover, since hydriodic acid is formed in each reaction, the first should be an example of autocatalytic acceleration and the second one of autocatalytic retardation.

The present communication deals with the investigation of the mechanism of the first reaction, and it is hoped to present a further communication dealing with that of the second.

Preliminary qualitative experiments have partly confirmed the foregoing supposition, inasmuch as the oxidation of hypophosphorous acid to phosphorous acid by iodine has been found to be catalytically accelerated by hydrogen ions.

Thus with hypophosphorous acid and iodine, the following results have been obtained. The numbers indicate the amount of substance in molecules per litre:

Hypophosphorous acid.	Iodine.	HCl.	Sodium acetate.	Remarks.
0·05	0·005	0·2	0·0	Reaction complete in 19 minutes, proceeded one-third in about 5 minutes.
0·05	0·005	0·0	0·2	Reaction proceeded one-third after 10 days = 14,400 minutes.

It will thus be seen that by the replacement of 0·2*N* hydrochloric acid by means of what is practically 0·05*N* hydrochloric acid, the velocity of the reaction is diminished in the ratio $\frac{1}{2880}$, which is of the same order of magnitude as the ratio of the corresponding concentrations of hydrogen ions.

With phosphorous acid, on the other hand, the following numbers were obtained:

H_3PO_3.	Iodine.	Sodium acetate.	Remarks.
0·2	0·02	0·0	Reaction complete in 7 days.
0·2	0·02	0·4	Reaction complete in 7 minutes.

From this it is evident that this reaction is enormously accelerated by removing or diminishing the hydrogen ion concentration. It has not been found possible to put to any real test the question as to whether it is the hypophosphorous ion or the undissociated molecule which undergoes oxidation, although certain considerations seem to point to the former as being the more probable.

The ionic nature of the reaction is indicated by experiments, described in the sequel, which have shown that it is the ionic and not the total concentration of the added acid which is of importance.

From the ionic standpoint, the reaction which has been investigated may be expressed as follows:

$$H_2PO_2' + I_2 + H_2O = HPO_3'' + 3H + 2I'.$$

The difficulty in investigating a reaction of this nature consists chiefly in the determination of the concentration of the various ions which take part in the reaction. If we are dealing with dilute solutions of the strong electrolytes, we may with safety assume the ionic to be equal to the total concentration, but such an approximation is not justified for any but the most dilute solutions of hypophosphorous acid. In experiments in which more concentrated solutions have been employed, the difficulty has been to some extent overcome by using a quantity of iodine sufficient to react with only about a tenth of the hypophosphorous acid. The resulting change in concentration of a fifth-normal solution is such that at the close of the experiment the concentration of acid has been reduced from $0·2N$ to $0·18N$, and over a range of concentration so small as this it may be safely assumed that the ionic is proportional to the total concentration.

The influence of the added acid on the degree of ionisation of the hypophosphorous acid is probably slight, and in the calculations which follow, this influence has been neglected on account of the complication which would be introduced into the integration of the velocity equation by any attempt to take it into consideration. The velocity of the reaction was measured under widely differing conditions at a temperature of 18°, and a few experiments were also carried out at 25°.

The course of the reaction was followed by titrating the residual iodine with a $N/50$ solution of sodium thiosulphate. Considerable difficulty was experienced in preparing pure hypophosphorous acid. The elimination of traces of foreign acids was especially important on account of their influence on the velocity coefficient.

For the purposes of the present investigation, the best test of the purity of a given sample of hypophosphorous acid has been found to be the velocity coefficient of its oxidation by iodine. For example, each of three different samples of the acid which had been purified by various methods, and in which it was difficult to detect any impurities, was found to undergo oxidation at a different rate.

The following succession of operations has been found to yield an acid which, according to the foregoing test, may be considered as pure.

Barium hypophosphite was prepared in the usual manner by boiling a mixture of barium hydroxide and phosphorus. The salt was precipitated from the filtered solution by the addition of alcohol, redissolved in water, and again precipitated by alcohol. It was then dissolved in the smallest possible quantity of cold water and allowed to crystallise slowly in a vacuum desiccator.

The purified barium salt was decomposed by dilute sulphuric acid, care being taken to avoid the use of any excess of acid. The barium sulphate was then removed by filtration, and the solution of hypophosphorous acid was evaporated in a vacuum at a low temperature to a thick syrup, which was caused to crystallise by immersion in a freezing mixture. The crystals were separated and thrice recrystallised.

Two such samples were prepared and have been used for the experiments.

The Influence of the Iodine Concentration.

If we assume that the velocity of the reaction is proportional to the concentration of the hydrogen ions, the velocity will be given by the equation

$$\frac{dx}{dt} = ka^m b^n h \ldots\ldots (1),$$

where a represents the concentration of the hypophosphorous acid ; b the concentration of the iodine ; h, the quantity of iodine hydrogen ions, and x the quantity of iodine which has disappeared at the time t.

In accordance with the equation previously given, it was anticipated that m would be equal to $n = 1$. This expectation has not been realised ; instead, it has been found that $m = 1$ and $n = 0$.

The proof that $n = 0$, in other words, that the velocity is independent of the iodine concentration, is as follows.

If the concentration of the hypophosphorous acid is made large compared with that of the iodine, the concentration of the former does not sensibly alter during the course of the reaction, and the equation (1) takes the form

$$\frac{dx}{dt}=k'.b^n,$$

where $k'=ka^mh$; if $n=1$, the reaction would be unimolecular, and on integrating we get

$$k'=\frac{1}{t}\log\frac{b}{b-x}.$$

If, on the other hand, $n=0$, the expression becomes $\frac{dx}{dt}=k'$, or $k'=\frac{x}{t}$, or, since $k'=ka^mh$, $k=\frac{x}{a^mht}$.

Several experiments were carried out under the foregoing conditions, and the value of the expression $\frac{1}{t}\log\frac{b}{b-x}$ was in all cases found to vary between wide limits.

The ratio $\frac{x}{t}$, on the other hand, was found to be practically constant until 90 per cent. of the iodine had disappeared.

The constancy of this ratio $\frac{x}{t}$ for these experiments is clearly brought out by the straight line which is shown in curve 1 in the figure, and also by the following typical experiment.

TABLE I.—*Experiment I.*

Hypophosphorous acid, $a=g$ mols. per litre $=0·10$.
Iodine...................... b „ „ „ 0·01.

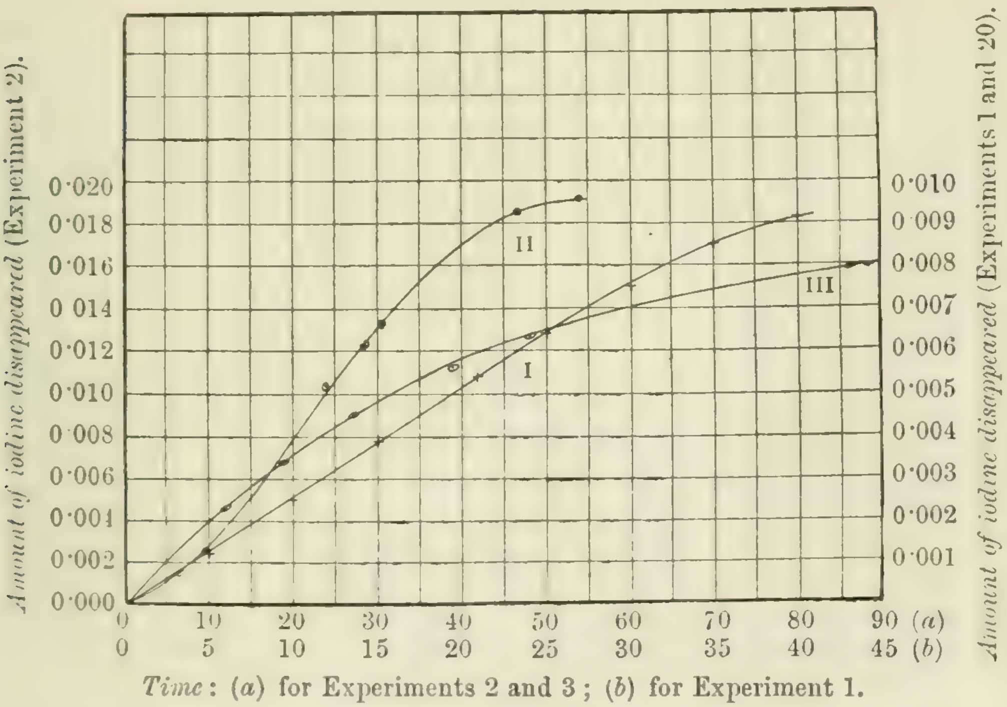
t = time in minutes; x = No. of c.c. of $0·01N$ sodium thiosulphate required to react with 5 c.c. of the mixture.

t.	x.	$K=x/t$.
5	0·60	[0·12]
10	1·26	0·126
15	1·93	0·128
21	2·68	0·127
25	3·21	0·128
30	3·74	0·125
35	4·23	0·121
40	4·52	[0·113]
200	4·77	—

A number of similar experiments have been carried out with the object of testing this point, and all have confirmed the conclusion that the velocity of the reaction during nine-tenths of its course is unaffected by the concentration of the iodine. During the last tenth of the reaction the measurements, as far as they can be considered trustworthy, indicate that the reaction with very low iodine concentrations is unimolecular with respect to the iodine.

Homogeneous reactions in which the velocity is independent of the concentration of one of the reacting substances are of rare occurrence.

A case is described by Friend (Trans., 1906, **89**, 1096), who studied the reaction between hydrogen peroxide and potassium persulphate, and found that the velocity was independent of the concentration of the peroxide provided that the latter was present in excess. This kind of behaviour is usually attributed to complications due to the occurrence of consecutive reactions, and Friend explained his results by assuming the occurrence of an intermediate compound the velocity of formation of which was very large compared with the velocity of its subsequent decomposition. That a similar explanation cannot be offered for the reaction under investigation will be evident from the following considerations. If we assume that an intermediate addition compound is formed according to the scheme for the following reversible reaction: $H_3PO_2 + I_2 = H_3PO_2I_2$, the compound subsequently reacting with water, thus: $H_3PO_2I_2 + H_2O = H_3PO_3 + 2HI$, and if *a*, *b*, and *c* represent the active masses of the hypophosphorous acid, iodine, and additive compound respectively, it follows from the law of mass action that $c = Kab$, and if a is large compared with b then $Ka = K'$ and $c = K'b$, hence the velocity of decomposi-



Curve I: Experiment 1. Curve II: Experiment 2. Curve III: Experiment 20.

tion of the intermediate compound would be independent of the hypophosphorous acid concentration and proportional to that of the iodine, exactly the reverse of what has been actually found.

The following hypothesis is capable of adequately expressing the observed facts. It is obvious that the reaction occurs in at least two stages, of which one is very much faster than the other (or others); furthermore, the iodine does not take part in the slower or controlling reaction.

We can split up the equation

$$H_2PO_2{}' + I_2 + H_2O = HPO_3{}'' + 3H^{\cdot} + 2I'$$

into two stages as follows:

$$(1)\ H_2PO_2{}' + H_2O = HPO_3{}'' + 3H^{\cdot} + 2\ominus$$
$$(2)\ 2H^{\cdot} + I_2 + 2\ominus = 2H^{\cdot} + 2I'.$$

Since the progress of the first of these reactions is accompanied by the production of hydrogen ions, the reaction cannot proceed unless some substance is present which can form anions to act as partners. If the rate of the former reaction is very slow compared with the rate at which iodine molecules can be converted into iodine ions, the velocity of the whole reaction will necessarily be independent of the iodine concentration.

A second mode of representing the above reaction might suppose the formation of a hydrated hypophosphorous ion or molecule which might undergo intermolecular change and then break up into hydrogen ions and phosphorous ions, thus:

$$H_2PO_2{}' + H_2O = H_4PO_3{}'$$
$$H_4PO_3{}' = HPO_3{}'' + 3H^{\cdot} + 2\ominus.$$

Either mode of representation would lead to the same conclusion with regard to the iodine.

The Influence of the Concentration of Hypophosphorous Acid.

Since the velocity of oxidation of hypophosphorous acid by iodine is increased by the hydrogen ions which are formed during the progress of the reaction, the ordinary methods cannot be used for determining the value of the exponent m in the equation:

$$\frac{dx}{dt} = ka^m h.$$

Taking into consideration this autocatalysis, the velocity, if we assume that $m = 1$, is given by the equation:

$$\frac{dx}{dt} = k_0(A - x)k_1h(A - x),$$

in which k_0 represents the velocity coefficient in the absence of hydrogen ions; k_1 the coefficient for the catalytically accelerated reaction; A

the initial concentration of the hypophosphorous acid, and h the concentration of the hydrogen ions.

Since the reaction practically comes to a standstill in alkaline or acetic acid solution, that is, in the absence of any considerable quantity of hydrogen ions, the first term in this equation may be neglected. If we put in the values for the hydrogen ion concentration, the equation then takes the form :

$$\frac{dx}{dt} = K_1(A - x)[\alpha(A - x) + \alpha'x + \alpha''c + \alpha'''2x] ;$$

(1) where $(A - x)$ represents the concentration of the hypophosphorous acid ; (2) where x represents the concentration of the phosphorous acid ; (3) where c represents the concentration of the added hydrochloric acid ; (4) where $2x$ represents the concentration of the hydriodic acid formed, and α, α', α'', and α''' are the corresponding ionisation coefficients.

The equation can be simplified if we make the not improbable assumption that the ionisation coefficients of the two weaker acids are equal,* and if we put $\alpha''' = 1$ when it takes the form

$$\frac{dx}{dt} = k_1(A - x)(\alpha A + \alpha''c + 2x),$$

which on integration gives

$$2k' = \frac{2\cdot30}{(C + a)t}\log_{10}\frac{a(C + x)}{C(a - x)},$$

where $C = \frac{\alpha A + \alpha''c}{2}$ = half the initial concentration of hydrogen ions.

In the absence of added acid, $C = \frac{\alpha A}{2}$, and for experiments in which A is less than B, the iodine concentration, $2x$ can become much greater than αA ; consequently the velocity should steadily increase as hydrogen ions accumulate in the mixture and pass through a maximum, afterwards decreasing in the usual manner. This behaviour which is characteristic of autocatalysis is shown clearly by experiment II (curve 2).

In this and subsequent tables, t represents the time expressed in minutes ; x the amount of iodine which has disappeared at the time t ; x being expressed in gram-molecules per litre, and in the last column are given the values of the expression :

$$2k_1 = \frac{2\cdot3}{(C + a)t}\log_{10}\frac{a(C + x)}{C(a - x)} .$$

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* From the data given by Kohlrausch and Holborn the coefficients of ionisation of hypophosphorous and phosphorous acids for an $N/100$ solution are 0·88 and 0·84 respectively. Strictly speaking, the α''' should be put equal to α''. This, however, considerably complicates the equation, and, practically, it makes no difference in the subsequent calculations if α''' is 1 or 0·9.

The value of a for a $N/50$ solution of hypophosphorous acid is given by Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*) as 0·85. If this value is used in calculating the constant for experiment II, very variable results are obtained. It was therefore necessary to evaluate the apparent initial concentration of the hydrogen ions before k_1 could be calculated. The evaluation was done by differentiating the expression $\frac{dx}{dt} = k_1(a A + 2x)(A - x)$, and on equating the resulting expression to zero we get $\frac{a A}{2} = A - 2x$.

The value of x at the point of maximum velocity was determined graphically, and it was thus found that for this particular experiment the apparent initial concentration of the hydrogen ions was 0·004, or $a = 0{\cdot}2$.

This calculation appears to indicate that at low concentrations of hypophosphorous acid only 0·2 of the total acid present is active as a catalyst, and the value of k_1 calculated on this assumption is almost identical with that obtained in more concentrated solutions when the ordinary values of a are employed.

TABLE II.—*Experiment II.*

Hypophosphorous Acid ….. … $A = 0{\cdot}02$.
Iodine ………………………. $B = 0{\cdot}0225$.

At point of maximum velocity $C = \frac{a A}{2} = 0{\cdot}002$.

∴ apparent $a = 0{\cdot}2$; (t = time in hours) ; temperature = 18°.

t.	x.	$A - x$.	$C + x$.	$2k_1$.
6·5	0·0015	0·0185	0·0035	[0·074]
9·5	0·0026	0·0174	0·0046	0·0773
24·0	0·0104	0·0096	0·0124	0·0803
28·5	0·0123	0·0077	0·0143	0·0775
30·5	0·0133	0·0067	0·0153	0·0776
46·75	0·0185	0·0015	0·0205	0·0791
54·0	0·0191	0·0009	0·0211	0·0765
			Mean =	0·0774

∴ $k_1 = 0{\cdot}0387$ if $a = 0{\cdot}02$.

It must be pointed out, however, that although in this and a few other experiments the proportion of catalytically active hydrogen ions appears to be diminished, it is possible that this is due at least partly to the fact that in these dilute acid solutions the velocity of the oxidation of the produced phosphorous acid to phosphoric acid is about one-tenth instead of a hundredth of the velocity of oxidation of the hypophosphorous acid. Further experiments at low concentrations have been deferred until the exact influence of this possible disturbing cause has been determined.

If considered in conjunction with experiments which will be described later (series *B*) and in which varying quantities of hydrochloric acid were added, experiment II confirms the supposition that the reaction is unimolecular with respect to the hypophosphorous acid.

In the following experiments (series *A*) the concentration of iodine was similar to that used in experiment II, that of the hypophosphorous acid being considerably larger. These experiments were intended to determine the magnitude of the constant k_1 in the absence of added acid.

Series A.

TABLE III.—*Experiment III.*

Hypophosphorous Acid .... $A = 0·05$.
Iodine .... $B = 0·01$.

$$\alpha = 0·67\,;\ C = \frac{\alpha A}{2} = 0·0155\,;\ \text{temperature} = 18°.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.	$x/\alpha A^2 t$.
10	0·00052	0·0495	0·0160	0·070	0·031
20	0·00112	0·0489	0·0166	0·071	0·0335
38	0·0021	0·0479	0·0176	0·071	0·033
61	0·0036	0·0464	0·0191	0·071	0·035
87	0·0047	0·0453	0·0202	[0·064]	0·0325
110	0·0059	0·0441	0·0214	[0·063]	—
			Mean =	0·071	

$$\therefore\ k_1 = 0·0355.$$

TABLE IV.—*Experiment IV.*

Hypophosphorous Acid .... $A = 0·10$.
Iodine .... $B = 0·02$.

$$\alpha = 0·62\,;\ \frac{\alpha A}{2} = C = 0·031\,;\ \text{temperature} = 18°.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.	$x/\alpha At$.
9	0·0022	0·0978	0·0332	0·0767	0·0405
19	0·0048	0·0952	0·0358	0·0761	0·0407
29	0·0082	0·0918	0·0392	0·0843	0·0453
43	0·0127	0·0873	0·0437	0·0851	0·0476
57	0·0169	0·0831	0·0479	0·0827	0·0476
65	0·0186	0·0814	0·0496	0·0800	—
69	0·0189	0·0811	0·0499	0·0760	—
77	0·0194	0·0806	0·0504	[0·069]	—
			Mean =	0·080	

$$\therefore\ k_1 = 0·040.$$

TABLE V.—*Experiment V.*

Hypophosphorous Acid .... $A = 0·10$.
Iodine .... $B = 0·01$.

$$a = 0·575\ ;\ \frac{aA}{2} = 0·0288 = C\ ;\ \text{temperature} = 18°.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.	x/aAt.
5	0·0012	0·0988	0·0300	0·080	0·041
9	0·0022	0·0978	0·0310	0·082	0·0425
15	0·0038	0·0962	0·0326	0·088	0·044
20	0·0052	0·0948	0·0340	0·089	0·045
25	0·0064	0·0936	0·0352	0·088	0·044
30	0·0078	0·0922	0·0366	0·084	—
40	0·0090	0·0910	0·0378	[0·071]	—
			Mean =	0·085	

$\therefore\ k_1 = 0·0425.$

TABLE VI.—*Experiment VI.*

Hypophosphorous Acid .... $A = 0·10$.
Iodine .... $B = 0·01$.

$$a = 0·576\ ;\ \frac{aA}{2} = C = 0·0288\ ;\ \text{temperature} = 18°.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.
5	0·0012	0·0988	0·0300	0·0867
10	0·0025	0·0975	0·0313	0·0856
15	0·0039	0·0961	0·0327	0·0885
21	0·0054	0·0946	0·0343	0·0860
25	0·0064	0·0936	0·0353	0·0850
30	0·0075	0·0925	0·0364	0·0822
35	0·0085	0·0915	0·0374	0·0785
40	0·0091	0·0909	0·0380	[0·0727]
			Mean =	0·085

$\therefore\ k_1 = 0·0425.$

TABLE VII.—*Experiment VII.*

Hypophosphorous Acid .... $A = 0·1$.
Iodine .... $B = 0·01$.

$$a = 0·595\ ;\ C = \frac{aA}{2} = 0·0288\ ;\ \text{temperature} = 18°.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.
6	0·0015	0·0985	0·0303	0·0825
11·5	0·0029	0·0971	0·0317	0·0820
16	0·0042	0·0958	0·0330	0·0827
22	0·0056	0·0944	0·0344	0·0810
27	0·0068	0·0932	0·0356	0·0790
32	0·0079	0·0921	0·0367	[0·077]
41	0·0091	0·0909	0·0379	—
			Mean =	0·082

$\therefore\ k_1 = 0·041.$

TABLE VIII.—*Experiment VIII.*

Hypophosphorous Acid .... $A = 0{\cdot}15$.
Iodine .... $B = 0{\cdot}01$.

$a = 0{\cdot}50$; $C = \frac{aA}{2} = 0{\cdot}0375$; temperature = 18°.

t.	x.	$A-x$.	$C+x$.	$2k_1$.	x/aA^2t
3	0·0009	0·1491	0·0384	[0·0528]	—
6	0·0029	0·1471	0·0404	0·0825	0·0433
9	0·0048	0·1452	0·0423	0·0890	0·0444
12	0·0065	0·1435	0·0440	0·090	0·0480
15	0·0079	0·1421	0·0454	0·087	0·0468
18	0·0087	0·1413	0·0462	0·081	—
			Mean =	0·086	

$\therefore\ k_1 = 0{\cdot}043$.

TABLE IX.—*Experiment IX.*

Hypophosphorous Acid .... $A = 0{\cdot}20$.
Iodine .... $B = 0{\cdot}02$.

$a = 0{\cdot}475$; $C = \frac{aA}{2} = 0{\cdot}0475$; temperature = 18°.

t.	x.	$A-x$.	$C+x$.	$2k_1$.	x/aA^2t.
3·5	0·0024	0·1975	0·0499	[0·069]	[0·0361]
5·5	0·0043	0·1957	0·0518	0·0797	0·041
7	0·0057	0·1943	0·0532	0·0803	0·0427
9·5	0·0073	0·1927	0·0548	0·0770	0·0405
11	0·0081	0·1919	0·0556	0·0730	0·0387
13	0·0083	0·1917	0·0558	[0·062]	—
			Mean =	0·078	

$\therefore\ k_1 = 0{\cdot}039$.

TABLE X.—*Experiment X.*

Hypophosphorous Acid .... $A = 0{\cdot}10$.
Iodine .... $B = 0{\cdot}01$.

$a = 0{\cdot}575$; $C = \frac{aA}{2} = 0{\cdot}0288$; temperature = 25°.

t.	x.	$A-x$.	$C+x$.	$2k_1$.	x/aA^2t.
2·5	0·0014	0·0986	0·0302	0·186	0·097
5·5	0·0032	0·0968	0·0320	0·194	0·099
8	0·0047	0·0953	0·0335	0·193	0·102
11	0·0063	0·0937	0·0351	0·185	0·099
14	0·0079	0·0921	0·0367	0·178	0·101
17	0·0088	0·0912	0·0376	[0·163]	—
20	0·0093	0·0907	0·0381	[0·147]	—
			Mean =	0·188	

$\therefore\ k_1 = 0{\cdot}094$.

TABLE XI.—*Experiment XI.*

Hypophosphorous Acid........ $A = 0{\cdot}025$.
Iodine .... $B = 0{\cdot}0025$.

$a = 0{\cdot}68$; $C = \frac{a\,A}{2} = 0{\cdot}0085$; temperature = 25°.

t.	x.	$A - x$.	$C + x$.	$2k_1$.
11	0·00019	0·02482	0·00868	[0·074]
41	0·00083	0·02417	0·00933	0·090
69	0·00142	0·02358	0·00992	0·093
87	0·00177	0·02323	0·01027	0·090
111	0·00220	0·02280	0·01070	0·087
			Mean =	0·090

$\therefore\ k_1 = 0{\cdot}045$.

TABLE XII.—*Experiment XII.*

Hypophosphorous Acid .... $A = 0{\cdot}01$.
Iodine .... $B = 0{\cdot}001$.

$a = 0{\cdot}85$; $C = \frac{a\,A}{2} = 0{\cdot}00425$; temperature = 25°.

t.	x.	$A - x$.	$C + x$.	$2k_1$.
28	0·000028	0·00994	0·00431	[0·0594]
71	0·000138	0·00986	0·00439	0·048
115	0·000237	0·00976	0·00446	0·052
171	0·00036	0·00964	0·00461	0·050
226	0·00046	0·00954	0·00471	0·047
323	0·00066	0·00934	0·00491	0·046
			Mean =	0·049

$\therefore\ k_1 = 0{\cdot}0245$.

In all these experiments the constant has been calculated both from the expression

$$2k_1 = \frac{2{\cdot}3}{(C + A)t} \log_{10} \frac{A(C + x)}{C(A - x)},$$

and also from the expression $k_1 = \frac{x}{a\,A^2 t}$.

The values obtained by the former calculation are given in column 5, those obtained by the latter in column 6, of the tables.

The relation $k_1 = \frac{x}{a\,A^2 t}$ is derived from the velocity equation

$$\frac{dx}{dt} = k_1(A - x)(a\,A + 2x)$$

by making the approximation that x is small compared with A and can be neglected ; it follows therefore that $\frac{dx}{dt} = k_1 A\,a\,A$ or $k_1 = \frac{x}{a\,A^2 t}$.

This expression accounts for the constancy of the ratio of $x : t$ which has been noticed in experiment I, and which is shown also in the majority of the experiments of series A.

TABLE XIII.

Summary of Experiments (II to XII) in which no Hydrochloric Acid was added.

No. of expt.	Temperature.	Hypophosphorous acid. A.	Iodine. B.	Ratio $A : B$.	k_1.	x/aA^2t.
2	18°	0·01	0·0125	0·8	0·039	—
3	,,	0·05	0·01	5·0	0·0355	0·033
4	,,	0·10	0·02	5·0	0·040	[0·041—0·047]
5	,,	0·10	0·01	10·0	0·0425	0·043
6	,,	0·10	0·01	10·0	0·0425	0·042
7	,,	0·10	0·01	10·0	0·041	—
8	,,	0·15	0·01	15·0	0·043	0·046
9	,,	0·20	0·01	20·0	0·039	0·0405
10	25	0·10	0·01	10·0	0·095	0·099
11	,,	0·025	0·0025	10·0	0·045	—
12	,,	0·01	0·001	10·0	0·0245	—

The correctness of this explanation of the constancy of the ratio $\frac{x}{t}$ is shown by the close agreement between the values of k_1 from columns 5 and 6.

Experiments III to IX were carried out at a temperature of 18°, and the three experiments, V, VI, and VII, although similar, are all given in full on account of the fact that they show clearly both the purity of the hypophosphorous acid and also its stability.

Experiments V and VI were carried out with two different samples of acid, both of which had been treated as already described. Experiment VII was carried out with the same sample of acid as experiment V, but after the lapse of more than six months, during which the stock solution of acid had been kept in an ordinary stoppered bottle. The slight difference in the value of k' may be due to slight oxidation of phosphorous to phosphoric acid, but it is more probably to be attributed to the experimental errors. It will be noticed that with the exception of experiment IX the slight variations of k_1 point to a lower value for this constant in the more dilute solutions.

In the same way, experiments X, XI, and XII, which were carried out at 25°, appear to confirm the conclusion already drawn from experiment I, namely, that at low concentrations of hypophosphorous acid the reaction proceeds with a diminished velocity; it behaves, in short, as though some of the hydrogen ions had become catalytically inactive. A possible interpretation of this result is that the reaction is of a higher order than the first.

All other experiments, however, confirm the conclusion that only one molecule of hypophosphorous acid takes part in the reaction, and the experiments which are summarised in Table XII emphasise the fact that the reaction velocity is independent of the iodine concentration.

Experiments with Added Acid.

In order to determine the influence of the hydrogen ion concentration on the reaction velocity, experiments (series *B*) were carried out in which a slight excess of iodine was used together with varying quantities of hydrochloric acid. In these experiments, the concentration of the hydrogen was given by the following expression: $(H^{\cdot}) = (\alpha A + \alpha' c + 2x)$; *c* being the molecular concentration of the added hydrochloric acid and α' its ionisation coefficient.

The constant $2k_1$, which is given in the following tables, was calculated from the usual equation, in which $C = \frac{\alpha A + \alpha' c}{2}$.

The results of this series of experiments are summarised in Table XXV, and a typical experiment is plotted in the figure (experiment XX, curve 3).

It will be noticed that for experiments in which $C = 0{\cdot}20$ or more, k_1 has a practically constant value, about 0·053, whereas for $C = 0{\cdot}10$ k_1 is about 20 per cent. lower, and approximates closely to the value found in series *A*. In order to check this conclusion, a number of experiments have been repeated, and for such duplicate experiments the constant only, and not the whole experiment, has been given.

Series B. Experiments XIII to XXIV. Temperature = 18°.

TABLE XIV.—*Experiment XIII.*

Hypophosphorous Acid ...... $A = 0{\cdot}0097$.
Iodine .... $B = 0{\cdot}0125$.
Hydrochloric Acid .... $c = 0{\cdot}10$.

$$\alpha = 0{\cdot}85\ ;\ \alpha' = 0{\cdot}93\ ;\ C = \frac{\alpha A + \alpha' c}{2} = 0{\cdot}0507.$$

t.	*x.*	*A − x.*	*C + x.*	$2k_1$.
20	0·00068	0·0090	0·0514	[0·0712]
48	0·0019	0·0078	0·0526	0·0872
84	0·0028	0·0069	0·0535	0·0775
119	0·0041	0·0056	0·0548	0·0867
156	0·0050	0·0047	0·0557	0·0870
225	0·0064	0·0033	0·0571	0·0875
306	0·0070	0·0027	0·0577	0·0760
332	0·0077	0·0020	0·0584	0·0860
			Mean =	0·0850

$\therefore k_1 = 0{\cdot}0425$.

Experiment 14, which is a duplicate of No. 13, gives $k_1 = 0{\cdot}040$.

TABLE XV.—*Experiment XV.*

Hypophosphorous Acid ...... $A = 0{\cdot}0098$.
Iodine .... $B = 0{\cdot}0125$.
Hydrochloric Acid .... $c = 0{\cdot}20$.

$$a = 0{\cdot}85\ ;\ a' = 0{\cdot}9\ ;\ C = \frac{aA + a'c}{2} = 0{\cdot}0947.$$

t.	x.	$A-x$.	$C+x$.	$2k_1$.
10	0·00076	0·00904	0·09546	[0·083]
20	0·00150	0·0083	0·0960	[0·083]
34	0·0029	0·0069	0·0976	0·106
50	0·0038	0·0060	0·0985	0·100
64	0·0047	0·0051	0·0994	0·104
79	0·0053	0·0045	0·1000	0·100
96	0·0060	0·0038	0·1007	0·100
131	0·0071	0·0027	0·1018	0·099
157	0·0077	0·0021	0·1024	0·098
216	0·0085	0·0013	0·1032	[0·093]
			Mean =	0·101

$\therefore k_1 = 0{\cdot}0505$.

Experiment 16, which is a duplicate of No. 15, gives $k_1 = 0{\cdot}051$.

TABLE XVI.—*Experiment XVII.*

Hypophosphorous Acid ...... $A = 0{\cdot}0095$.
Iodine .... $B = 0{\cdot}0125$.
Hydrochloric Acid .... $c = 0{\cdot}30$.

$$a = 0{\cdot}85\ ;\ a' = 0{\cdot}89\ ;\ C = \frac{aA + a'c}{2} = 0{\cdot}1377.$$

t.	x.	$A-x$.	$C+x$.	$2k_1$
7	0·0010	0·0085	0·1387	0·114
15	0·0019	0·0076	0·1396	0·108
23	0·0030	0·0065	0·1407	0·117
39	0·0042	0·0053	0·1419	0·107
53	0·0053	0·0042	0·1430	0·109
68	0·0062	0·0033	0·1439	0·110
84	0·0067	0·0028	0·1444	0·102
114	0·0076	0·0019	0·1453	0·099
139	0·0082	0·0013	0·1459	0·100
198	0·0088	0·0007	0·1465	[0·091]
			Mean =	0·107

$\therefore k_1 = 0{\cdot}0535$.

Experiment 18, which is a duplicate of No. 17, gives $k_1 = 0{\cdot}0535$.

TABLE XVII.—*Experiment XIX.*

Hypophosphorous Acid …… $A = 0{\cdot}0096$.
Iodine ………………… ….. $B = 0{\cdot}0125$.
Hydrochloric Acid ……….. $c = 0{\cdot}40$.

$$\alpha = 0{\cdot}85\ ;\ \alpha' = 0{\cdot}88\ ;\ C = \frac{\alpha A + \alpha' c}{2} = 0{\cdot}1803.$$

t.	*x.*	*A − x.*	*C + x.*	$2k_1$.
6	0·0009	0·0087	0·1812	[0·096]
15	0·0025	0·0071	0·1828	0·110
23	0·0034	0·0062	0·1837	0·103
36	0·0047	0·0049	0·1850	0·101
48	0·0059	0·0037	0·1862	0·108
61	0·0066	0·0030	0·1869	0·103
74	0·0071	0·0025	0·1874	0·098
99	0·0079	0·0017	0·1882	[0·094]
124	0·0083	0·0013	0·1886	[0·087]
			Mean =	0·103

$\therefore k_1 = 0{\cdot}0515$.

TABLE XVIII.—*Experiment XX.*

Hypophosphorous Acid …… $A = 0{\cdot}00946$.
Iodine …………………….. $B = 0{\cdot}0125$.
Hydrochloric Acid ……….. $c = 0{\cdot}50$.

$$\alpha = 0{\cdot}85\ ;\ \alpha' = 0{\cdot}87\ ;\ C = \frac{\alpha A + \alpha' c}{2} = 0{\cdot}2218.$$

t.	*x.*	*A − x.*	*C + x.*	$2k_1$.
5	0·00105	0·00841	0·2228	0·106
12	0·0023	0·00716	0·2241	0·103
19	0·0034	0·00606	0·2252	0·104
27	0·0045	0·00496	0·2263	0·107
39	0·0056	0·00386	0·2274	0·102
48	0·0063	0·00316	0·2281	0·102
93	0·0081	0·00136	0·2299	[0·092]
			Mean =	0·104

$\therefore k_1 = 0{\cdot}052$.

TABLE XIX.—*Experiment XXI.*

Hypophosphorous Acid .. … $A = 0{\cdot}0194$.
Iodine …………………….. $B = 0{\cdot}025$.
Hydrochloric Acid ……….. $c = 0{\cdot}20$.

$$\alpha = 0{\cdot}8\ ;\ \alpha' = 0{\cdot}9\ ;\ C = \frac{\alpha A + \alpha' c}{2} = 0{\cdot}098.$$

t.	*x.*	*A − x.*	*C + x.*	$2k_1$.
11	0·0022	0·0172	0·1002	0·105
28	0·0054	0·0140	0·1034	0·113
50	0·0087	0·0107	0·1067	0·114
70	0·0110	0·0084	0·1090	0·114
90	0·0127	0·0067	0·1107	0·111
115	0·0145	0·0049	0·1125	0·112
140	0·0159	0·0035	0·1139	0·113
212	0·0178	0·0016	0·1158	0·107
			Mean =	0·111

$\therefore k_1 = 0{\cdot}0555$.

TABLE XX.—*Experiment XXII.*

Hypophosphorous Acid …… $A = 0·0195$.
Iodine ……………………… $B = 0·025$.
Hydrochloric Acid ………… $c = 0·040$.

$$a = 0·80\ ;\ a' = 0·88\ ;\ C = \frac{aA + a'c}{2} = 0·184.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.
17	0·0056	0·0139	0·1896	0·113
24	0·0072	0·0123	0·1912	0·107
37	0·0105	0·0090	0·1945	0·113
48	0·0128	0·0067	0·1968	0·118
55	0·0134	0·0061	0·1974	0·111
76	0·0157	0·0038	0·1997	0·112
115	0·0176	0·0019	0·2016	0·107
			Mean =	0·111

$\therefore k_1 = 0·0555$.

Experiment 23, which duplicates No. 22, gives $k_1 = 0·0535$.

TABLE XXI.—*Experiment XXIV.*

Hypophosphorous Acid ……… $A = 0·05$.
Iodine ………………………… $B = 0·005$.
Hydrochloric Acid …………… $c = 0·20$.

$$a = 0·65\ ;\ a' = 0·90\ ;\ C = \frac{aA + a'c}{2} = 0·1563.$$

t.	x.	$A - x$.	$C + x$.	$2k_1$.	$x/A(a + Aa'c)t$.
3	0·00170	0·04830	0·1080	0·106	0·0535
6·5	0·00376	0·04624	0·1101	0·111	0·0545
9	0·00520	0·0448	0·1115	0·111	0·0545
12	0·00638	0·0436	0·1127	0·105	0·0502
16	0·00728	0·0427	0·1136	[0·089]	—
19	0·00763	0·0424	0·1140	—	—
			Mean =	0·108	
		$\therefore k_1 = 0·054$.			0·0535

TABLE XXII.

Summary of Experiments with added Hydrochloric Acid. Series B.

No. of expt.	Hypophosphorous acid.	Iodine.	HCl.	k_1.
13	0·01	0·0125	0·10	0·0425
14	0·01	0·0125	0·10	0·0400
15	0·01	0·0125	0·20	0·0505
16	0·01	0·0125	0·20	0·051
17	0·01	0·0125	0·30	0·0535
18	0·01	0·0125	0·30	0·0535
19	0·01	0·0125	0·40	0·0515
20	0·01	0·0125	0·50	0·0520
21	0·02	0·025	0·20	0·0555
22	0·02	0·025	0·30	0·0555
23	0·02	0·025	0·30	0·0535
24	0·05	0·005	0·20	0·053

It will be seen that the lower value of k_1 for experiment XIII is confirmed by experiment XIV; the higher values for experiments XV, XVII, and XXII are confirmed by experiments XVI, XVIII, and XXIII.

It is evident that the reaction velocity is strictly proportional to the total concentration of hydrogen ions for concentrations of hydrochloric acid greater than $0{\cdot}2N$.

The large value for k_1 from series B as compared with that obtained in series A might be attributed to the fact that more dilute solutions have been employed in series B.

Corresponding to this greater dilution, the ionisation of the hypophosphorous acid becomes increased, and the reaction, if it consisted in the oxidation of the ion and not of the undissociated molecule, would proceed relatively faster in the more dilute solutions.

If this supposition were correct, then the constants obtained in two experiments with different initial concentration of hypophosphorous acid should be related by the following equations:

$$\frac{a_2}{a_1} = \frac{k_2}{k_1}\,; \quad k_2 = k_1 \frac{a_2}{a_1}.$$

Taking experiment IV (series A), $k_4' = 0{\cdot}40$; $a = 0{\cdot}55$.
,, XVII (,, B), $k_{16}' = 0{\cdot}535$; $a = 0{\cdot}83$.

$$k_{16} = \frac{k_4 \times 083}{0{\cdot}53} = 0{\cdot}0602 \text{ instead of } 0{\cdot}053.$$

This hypothesis fails then to express the quantitative relation between the two series of experiments.

That it also fails qualitatively is shown by the fact that experiments XIII and XIV, in which the initial concentration of hypophosphorous acid is low, have the value k' characteristic of series A, and also by the fact that experiment XXIV, which should give $k = 0{\cdot}040$, gives instead $k = 0{\cdot}053$.

The Temperature Coefficient.

The temperature coefficient of the velocity coefficient can be calculated from experiments V and X by means of the equation: $\log k = p + qt$, and since k at $18^\circ = 0{\cdot}043$ and k at $25^\circ = 0{\cdot}095$.

The coefficient per ten degrees rise in temperature is calculated to be $\frac{k_t + 10}{k_t} = 3{\cdot}1$.

Summary of Results.

(1) The velocity of the oxidation of hypophosphorous acid by iodine is independent of the concentration of iodine provided the latter is greater than about $0{\cdot}001N$. The limiting value of this concentration

appears to vary with the initial concentration of the hypophosphorous acid.

(2) The reaction is unimolecular with respect to the hypophosphorous acid, but it is catalytically accelerated by hydrogen ions.

(3) Since hydrogen ions are produced during the course of the reaction, the velocity, in the absence of any large initial concentration of acid, undergoes autocatalytic acceleration.

(4) The magnitude of the velocity coefficient k_1 appears to vary within narrow limits with the initial concentration of the hypophosphorous acid and of the added acid.

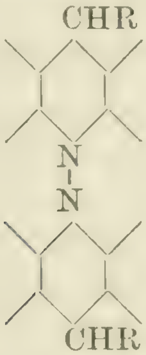
UNIVERSITY OF MELBOURNE.

CLVII.—*The Action of Bromine on 5-Phenylacridine and its Halogen Derivatives.*

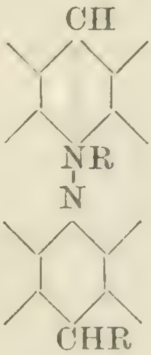
By ALBERT ERNEST DUNSTAN and THOMAS PERCY HILDITCH.

IN a communication on the addition of halogen to acridine and naphthacridine bases, Senier and Austin (Trans., 1904, **85**, 1196) bring forward evidence showing that the compounds formed are additive in nature, and that the addition of halogen takes place both at the meso-carbon and nitrogen atoms, in some cases rupturing the para-linking between them.

Typical instances are:

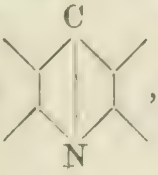


(I.)

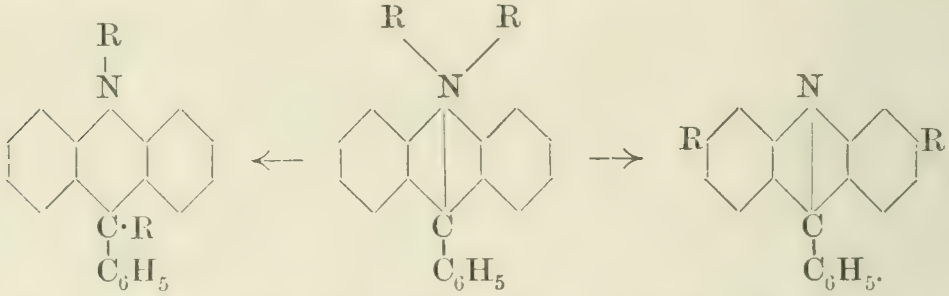


(II.)

;

R being halogen. It will be noticed that in (I) the typical acridine fluorophore, , is absent, whilst in (II) it still persists, hence these two types of additive products are distinguishable according as fluorescence is present or not. The substances described by Senier and Austin were prepared by simple addition of the halogen to the base dissolved in cold anhydrous solvents. They are unstable in presence of water, and in some cases they lose halogen merely on prolonged boiling with acetone.

Dunstan and Oakley (*Ber.*, 1906, **39**, 981) described the action of halogens on 5-phenylacridine, obtaining a fluorescent dichloro-derivative by chlorination of the base in dry chloroform solution, and also by the action of bleaching powder on the hydrochloride of the base in aqueous solution. They also found that when 5-phenylacridine was brominated in boiling acetic acid solution with excess of halogen and a trace of iodine, a tribromo-derivative was isolated. Under such conditions, substitution is more probable than addition, especially when it is considered with what ease the nitro-group, for instance, enters the nucleus. It seems most likely that initially the halogen attaches itself in the way Senier and Austin suggest, but subsequently one or more of the added atoms may in the presence of excess of halogen either enter the ring or take up the para-meso-positions:



That some substitution does occur is rendered evident by the constant recurrence of the crystalline hydrobromide of phenylacridine from the various mother liquors after the separation of the main products.

The tribromo-derivative already alluded to was considered at first to be substituted entirely; but its fluorescence is notably less than that of the parent base, and, moreover, although unaffected by methyl iodide at 130°, it lost bromine (2 atoms) quite easily when boiled for ten minutes with methyl sulphate. The resulting solution was treated in the usual way with aqueous potassium iodide, but, instead of a methiodide, monobromophenylacridine was precipitated. As it is exceedingly improbable that methyl sulphate should eliminate halogen substituted in the acridine ring, we consider that the two displaced bromine atoms were attached at the meso-positions respectively, and that the stability of the substance is due primarily to the fact that the 5-phenyl group has a considerable influence on the meso-nitrogen atom (Dunstan and Stubbs, *Ber.*, 1906, **39**, 2402). Methyl iodide does, we believe, form a methiodide, but only with great difficulty, and precisely similar observations were made in the case of *p*-bromophenylacridine (*loc. cit.*).

In this connexion, we desire to draw attention to the steric hindrance displayed by the substitution of the para-hydrogen atom of the 5-phenyl group. Both 5-*p*-chloro- and 5-*p*-bromo-phenylacridine resist methylation to a considerable extent; no doubt this is due to the proximity of the meso-nitrogen atom to this position.

EXPERIMENTAL.

5-p-*Chlorophenylacridine.*—Eight grams of *p*-chlorobenzoic acid, 10 grams of diphenylamine, and 16 grams of anhydrous zinc chloride were heated to 180—200° in a reflux apparatus on an oil-bath during two days. The resulting green mass was extracted repeatedly with boiling methylated spirit, and the residue was further extracted with 4*N*-sulphuric acid. Each extract was treated with aqueous ammonia, which precipitated the crude base as a yellow powder. This was treated with aqueous ammonium chloride and with cold alcohol to remove traces of zinc hydroxide and of diphenylamine respectively. From the two extracts, 5 grams of the pure substance were obtained.

5-p-*Chlorophenylacridine* separates from boiling alcohol as a yellow, crystalline powder, sparingly soluble in cold alcohol or glacial acetic acid with a green fluorescence. It is readily soluble in cold concentrated sulphuric acid, giving an intense green fluorescence which is strongly inhibited on dilution, with concurrent hydrolysis. The substance does not melt below 270°:

0·1045 gave 0·3015 CO_2 and 0·0370 H_2O. C = 78·68; H = 3·94.
0·2458 „ 10·9 c.c. dry nitrogen at 15° and 755 mm. N = 5·28.
0·1701 „ 0·0863 AgCl. Cl = 12·55.
$C_{19}H_{12}NCl$ requires C = 78·76; H = 4·15; N = 4·84; Cl = 12·26 per cent.

This base was characterised by the following salts.

5-p *Chlorophenylacridine Platinichloride.*—This was prepared in the usual manner in alcoholic hydrochloric acid solution. It was a yellow, amorphous precipitate, which, after washing and drying at 100°, decomposed at 267—270°:

0·3062 gave 0·0599 Pt. Pt = 19·56.
$(C_{19}H_{12}NCl)_2,H_2PtCl_6$ requires Pt = 19·72 per cent.

5-p-*Chlorophenylacridine Chromate.*—This was prepared by precipitation of the alcoholic solution of the base with potassium chromate. After washing the yellow precipitate it was dried at 100°. It did not melt below 250°:

0·2007 gave 0·0205 Cr_2O_3. Cr = 6·99.
0·1943 ,, 0·0197 Cr_2O_3. Cr = 6·94.
$(C_{19}H_{12}NCl)_2,H_2CrO_4$ requires Cr = 7·46 per cent.

5-p-*Chlorophenylacridine Picrate.*—This beautifully crystalline, yellow compound was obtained by allowing a hot alcoholic solution of its generators to cool. It melts and decomposes at 230°:

0·0630 gave 5·5 c.c. dry nitrogen at 18° and 764 mm. N = 10·3.
$C_{19}H_{12}NCl,C_6H_3O_7N_3$ requires N = 10·8 per cent.

The base was methylated by being heated in a sealed tube to 130° during three hours with a slight excess of methyl iodide dissolved in methyl alcohol. After cooling and opening the tube, a dark red, crystalline *methiodide* was obtained. This was soluble in alcohol with slight fluorescence, due probably to a trace of the unmethylated base.

5-p-*Chlorophenylacridine methiodide* melts at 192°; potassium hydroxide precipitates a yellow, amorphous *carbinol* base from the alcoholic solution, whilst the solution in concentrated sulphuric acid exhibits intense green fluorescence:

0·1137 gave 3·2 c.c. dry nitrogen at 18° and 753 mm. and 0·0308 H_2O. N = 3·3; H = 3·04.
$C_{20}H_{15}NClI$ requires N = 3·48; H = 3·24 per cent.
0·0644 gave 0·0541 AgCl + AgI, whereas 0·0564 is required by theory.

The Action of Bromine on 5-p-*Chlorophenylacridine.*—One molecular proportion of the base was dissolved in excess of glacial acetic acid, two molecular proportions of bromine were slowly added, and a yellow precipitate appeared, which dissolved on the application of heat; no evolution of hydrogen bromide was noticed. The solution was boiled for a day in a reflux apparatus and, on cooling, poured into water, when a dark brown, crystalline mass was formed, which was collected and dried. This compound was crystallised from boiling toluene, and appeared as yellow needles which melted sharply at 176°. The toluene solution shows a dark green fluorescence, but the alcoholic solution exhibits only feeble fluorescence. In concentrated sulphuric acid, an intense fluorescence appears, which vanishes on dilution, with concurrent hydrolysis. Analysis showed that two atoms of bromine had been absorbed, but the results fail to indicate whether substitution or addition had taken place:

0·2856 gave 6·4 c.c. dry nitrogen at 18° and 758 mm. and 0·0626 H_2O. N = 2·64; H = 2·44.
$C_{13}H_{12}NClBr_2$ (addition) requires N = 3·11; H = 2·67 per cent.
$C_{19}H_{10}NClBr_2$ (substitution) ,, N = 3·13; H = 2·21 ,,
0·1100 gave 0·1290 AgCl + AgBr.
Theory requires 0·1277 AgCl + AgBr (substitution) or 0·1272 (addition).

This derivative was further characterised by the preparation of a yellow, amorphous *dichromate*, which softened between 200—205°, but had no definite melting point:

0·0900 gave 0·0122 Cr_2O_3. Cr = 9·29.
$(C_{19}H_{12}NClBr_2)_2,H_2Cr_2O_7$ requires Cr = 9·34 per cent.

It is to be noted, then, that this bromo-derivative is capable of forming salts, hence we consider that the halogen is not attached in such a way as to saturate the nitrogen valencies, but occupies the para-meso-position.

Methylation of Dibromo-5-p-*chlorophenylacridine.*—On methylation in the usual manner with a slight excess of methyl iodide dissolved in methyl alcohol, the heating being continued during four hours at 130°, a dark crystalline powder remained which, after being dried at 100°, gave analytical results indicating that addition of the reagent had taken place.

When, however, methyl sulphate was used, a substance was obtained after the usual extraction with boiling water, which crystallised in yellow needles and melted at 220°. This gave figures indicating that it was the *methosulphate* of the parent monochloro-base.

0·1811 gave 0·0942 $BaSO_4$. S = 7·15.
$C_{19}H_{12}NCl,(CH_3)_2SO_4$ requires S = 7·71 per cent.

The filtrate from this methosulphate was treated with aqueous potassium iodide and a bright yellow, crystalline precipitate appeared. After washing and drying, it melted at 195°, whereas the methiodide of 5-*p*-chlorophenylacridine prepared from methyl iodide and the base melted at 192°. Analysis again indicated that methylation by means of methyl sulphate had displaced two atoms of bromine. The methiodide is very soluble in alcohol, giving a slight green fluorescence, but in cold concentrated sulphuric acid it exhibits a deep green fluorescence which disappears on dilution.

Action of Bromine on 5-p-*Bromophenylacridine.*—5-*p*-Bromophenylacridine (Dunstan and Stubbs, *Ber.*, 1906, 39, 2402) was brominated in the same manner as was described above, when a brown, crystalline solid was obtained which, after purification, melted at 212°. It is sparingly soluble in alcohol, giving a yellow non-fluorescent solution, but it is freely soluble in cold concentrated sulphuric acid with a deep green fluorescence. The analytical numbers, again, do not distinguish between the alternative additive and substitutive formulæ:

0·2136 gave 4·7 c.c. dry nitrogen at 27° and 757 mm. and 0·0392 H_2O. N = 2·51; H = 2·04.
$C_{19}H_{12}NBr_3$ requires N = 2·83; H = 2·43 per cent.

This substance was characterised by its *dichromate* and *picrate*, both of which salts were prepared in the usual manner; the former is a bright yellow, amorphous powder which decomposes between 210—215°:

0·1061 gave 0·0130 Cr_2O_3. Cr = 8·39.

$(C_{19}H_{12}NBr_3)_2,H_2Cr_2O_7$ requires Cr = 8·62 per cent.

The *picrate* is a reddish-brown, crystalline powder which melts with profound decomposition at 255°:

0·0969 gave 6·65 c.c. dry nitrogen at 23° and 765 mm. and 0·0158 H_2O. N = 7·95; H = 1·81.

$C_{19}H_{12}NBr_3,C_6H_3O_7N_3$ requires N = 7·75; H = 2·07 per cent.

This bromo-derivative was heated with a slight excess of methyl iodide dissolved in methyl alcohol during three hours at 130°, when dark red crystals were obtained which, after being dried at 100°, turned scarlet. This substance, however, on analysis was found to be the unaltered tribromo-compound. Using methyl sulphate, a fluorescent solution was obtained after extraction with water. This gave no crystalline methosulphate, but addition of potassium iodide caused the precipitation of a yellow solid which, after purification, melted at 221—223°. It was sparingly soluble in alcohol with feeble fluorescence, but gave the usual deep green fluorescence with cold sulphuric acid. Potassium hydroxide precipitated a pale yellow solid from its solutions. Owing to the small amount of material available, satisfactory analytical results were not obtained. Methyl sulphate, therefore, acts on the tribromo-derivative in a similar manner to that described previously; it eliminates two atoms of bromine, but does not effect methylation.

Action of Bromine on 5-Phenylacridine.—Ten grams of 5-phenylacridine were dissolved in 100 c.c. of glacial acetic acid and 4 c.c. of bromine were added; a yellow precipitate was at once formed, which dissolved on the application of heat. The solution was heated to boiling during a day in a reflux apparatus and a steady elimination of hydrogen bromide was noticed. A mass of red crystals was deposited when the solution cooled, and on pouring the mother liquors into water a yellow precipitate appeared. These two products were separately purified by crystallisation from acetic acid, and each melted at 180°, whilst a mixed melting point determination gave the same result. The substance is soluble in alcohol or acetic acid with faint fluorescence, and a bright green fluorescence is exhibited by the solution in sulphuric acid. It was purified by crystallisation from boiling toluene, from which it separated in bright yellow needles:

0·3692 gave 6·4 c.c. dry nitrogen at 15° and 757 mm. N = 2·36.
0·3018 ,, 6·3 c.c. ,, ,, 14° ,, 757 mm. N = 2·50.
0·2220 ,, 0·2521 AgBr. Br = 48·3.

$C_{19}H_{12}NBr_3$ requires N = 2·83; Br = 48·6 per cent.

Tribromo-5-phenylacridine dichromate was prepared in the usual manner. It is a brown, amorphous powder which decomposes at 175°:

0·1250 gave 0·0167 Cr_2O_3. Cr = 9·15.

$(C_{19}H_{12}NBr_3)_2,H_2Cr_2O_7$ requires Cr = 8·62 per cent.

Tribromo-5-phenylacridine picrate was prepared by mixing hot alcoholic solutions of its generators. It crystallises in fine yellow needles which melt at 214°:

0·1092 gave 9·55 c.c. at 21° and 760 mm. and 0·0170 H_2O. N = 10·21; H = 1·73.

$C_{19}H_{12}NBr_3,2C_6H_3O_7N_3$ requires N = 10·1; H = 1·85 per cent.

Methylation of Tribromo-5-phenylacridine.

On treatment in the usual way with methyl iodide, no methylation took place; on being heated with methyl sulphate, however, the tribromophenylacridine was decomposed with evolution of bromine and hydrogen bromide. The heating was continued during half an hour, when the resulting mass was boiled with water, giving a deep green fluorescent solution from which no crystalline methosulphate could be isolated. When potassium iodide was added, a fine yellow, crystalline precipitate appeared which, after isolation, melted at 235°. It was readily soluble in alcohol, toluene, or dilute sulphuric acid with slight fluorescence, and in cold concentrated sulphuric acid giving a red solution showing an intense green fluorescence:

0·1442 gave 0·0822 AgBr. Br = 24·24.

$C_{19}H_{12}NBr$ requires Br = 23·95 per cent.

We therefore conclude that two atoms of bromine had been expelled by methyl sulphate, leaving monobromophenylacridine. This conclusion is supported by the fact that on boiling tribromophenylacridine with aqueous potassium hydroxide a reaction ensues and bromine can be detected in the solution.

To illustrate further the action of methyl sulphate on bromo-derivatives of 5-phenylacridine, we finally selected a monobromophenylacridine described by one of us with R. O'F. Oakley (*Ber.*, 1906, **39**, 981). This substance (m. p. 275°) was also treated with methyl sulphate, when a *methosulphate* was obtained which, after purification, gave the following results:

0·4702 gave 0·2443 $BaSO_4$. S = 7·11.

$C_{19}H_{12}NBr,(CH_3)_2SO_4$ requires S = 6·96 per cent.

This substance crystallised in stout, yellow prisms which melted at 210°. It is soluble in alcohol, toluene, or dilute sulphuric acid with no fluorescence, and in concentrated sulphuric acid with bright green fluorescence.

Hence there seems to be no doubt that the action of bromine on the phenylacridine nucleus is primarily additive, the added atoms occupying the para-meso-positions. We are led to this conclusion chiefly by the fact that salt formation is not inhibited as would be the case were the halogen atoms attached to the completely saturated meso-nitrogen. Further, the striking diminution of fluorescence points to the fact that the halogen in some way hampers the tautomeric swinging of linkings insisted upon by Hewitt in his explanation of acridine fluorescence; this would not be the case were the halogen simply substituted in the nucleus. It might be brought forward in objection to this argument that atoms substituted in the sensitive 2 : 8-positions would not be proof against replacement by such reagents as methyl sulphate, but against this we would urge that it is scarcely probable that bromine would be replaced by hydrogen.

The authors desire to thank Mr. F. B. Thole for his useful assistance.

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CLVIII.—*The Adsorption of Iodine by Carbon.*

By Oliver Charles Minty Davis.

Although the phenomena of adsorption have been known and studied for a century,* the investigators in this line have not yet come to an agreement as to a general theoretical explanation of the facts in question.

On the one hand, there is the theory of which Travers (*Proc. Roy. Soc.*, 1906, **78**, *A*, 9) is the most recent exponent, that adsorption consists exclusively of a more or less complete absorption into the interior of the solid. On the other hand, Freundlich has recently published a lengthy and important paper in which adsorption is regarded as exclusively a condensation on the surface.

In these circumstances, it might readily be conjectured that both surface condensation and diffusion into the interior of the solid phase would play a part in all cases of adsorption.

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* For references to the literature, see Ostwald's *Lehrbuch d. allgem. Chem.*, I, p. 778; II. 3. Lieferung I (2nd edition), and Freundlich, *Habilitationsschrift*, Leipzig, 1906. *Zeitsch. physikal. Chem.*, 1907, **57**, 385, also Freundlich and Losev, *Zeitsch. physikal. Chem.*, 1907, **59**, 284.

This indeed has been actually asserted by Küster (*Lehrbuch d. allgem. Chem.*, 1907, p. 314, but see p. 422. Compare Masson, *Proc. Roy. Soc.*, 1904, **74**, 230), and in the following investigation I have found this to be the case in the adsorption of iodine, dissolved in organic solvents, by charcoal.

It was formerly hoped that the laws of solution would satisfactorily explain the phenomena of adsorption. This hope was, however, doomed to failure, for the relationship between the concentration of the adsorbed substance in the fluid phase and the amount adsorbed by the solid, interpreted in the light of the theory of solid solution as a distribution ratio, leads to conclusions as to the molecular condition of the adsorbed substance which are often irreconcilable with our best established ideas of the value of molecular weights.

An example of this may be taken from Travers' experiments on the adsorption of hydrogen by cocoanut charcoal at the temperature of liquid air; there, such an interpretation would lead to the assumption that the molecular weight of the adsorbed hydrogen would be only a fraction of its usual atomic weight.

The difficulty thus arising is attributed by the adherents of the explanation by the theory of solid solution (Travers, *loc.cit.*) to the slowness, and hence incompleteness, of the process of diffusion into the solid phase; consequently, they argue, it is unfair to expect that the laws deduced for perfect equilibria (distribution ratio, &c.) should be directly applicable.

The Leipzig school hold, on the contrary, that adsorption is merely a particular application of Gibb's fundamental theorem, which predicts that, if presence of the dissolved substance in the surface between solid and fluid would diminish the surface energy, the substance would accumulate in that surface, the concentration in the meniscus being greater than that throughout the body of the fluid.

The converse proposition would explain Lagergren's observation of cases of negative adsorption.

It is evident that this theory, which admits of further important deductions confirmed by experiment, is correct as far as it goes.

It is, however, advanced in its most extreme and exclusive form by Freundlich, who says categorically,* "Denkt man sich eine ideale Trennungsfläche zwischen Kohle und Flüssigkeit und die Oberflächenschicht etwas nach beiden Seiten hineinragend, so möchte ich annehmen, dass die Veränderungen in der Konzentration *nur in dem der Flüssigkeit zugekehrten Teile der Oberflächenschicht* statt hat."

This he bases on the improbability of diffusion taking place, in the few minutes duration of the experiments, to even the depth of millionths of a millimetre.

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* *Habilitationsschrift*, p. 82. Italics by Freundlich.

He further adduces in support of this view a generalisation made by him, based on a somewhat scanty experimental material, that the adsorption, other things being equal, is independent of the nature of the adsorbing solid.

It is, however, a second important result of the present paper that this generalisation has not been confirmed in the case of carbon.

Unfortunately the necessary data for the numerical treatment of the surface tension are as yet insufficient to serve as a basis for more than a qualitative application of the general expression deduced by Freundlich. Even the order of magnitude of this effect (which must occur) has not yet been determined, and it is not known whether it could ever exert a measurable influence.

Formulæ to Represent Adsorption.

In order to further uniformity in the literature of the subject, Freundlich's notation has been adopted.

a is the original total amount of the solute before adsorption; a/v is thus the original concentration of the substance.

x is the amount adsorbed if m grams of solid are employed, therefore x/m is the amount adsorbed per gram.

$a-x$ is thus the amount left unadsorbed, and hence $\overline{a-x}/v=c$, the final concentration of the solution.

There are at present two formulæ employed to represent adsorption. The first:

$$\frac{x}{m} = \beta c^{\frac{1}{p}} \quad \text{(exponential formula)},$$

where β and p are constants, is an extension of Henry's law, with one side raised to a power $1/p$ in which p is found in practice to lie between 2 and 10. This formula, although known a priori to be imperfect (compare Freundlich, *loc. cit.*), nevertheless describes the phenomena very well. It is purely empirical and it is entirely devoid of theoretical basis.

The second formula:

$$\lambda = \frac{v}{m} \, ln \frac{a}{a-x} = \beta \left(\frac{a}{v}\right)^{\frac{1}{p}-1} \quad (\lambda\text{-formula}),$$

in which λ and p are constants, is an extension by Freundlich of an empirical formula introduced by Kroeker (*Dissertation*, Berlin, 1892; for an exposition and criticism, see the succeeding paper by McBain). The experimental data of the present paper have been calculated according to both formulæ.

Plan of the Investigation.

One simple substance, iodine, has been taken for study, and the nature of the solvent and the adsorbing agent have been systematically varied. The solvents employed were toluene, alcohol, ethyl acetate, benzene, and chloroform.

The adsorbing agents were animal, sugar, and cocoanut charcoal. It was proved in each case that no disturbing reactions took place under the experimental conditions chosen.

The object of the investigation was, in the first place, to carry out a series of crucial experiments which should definitely decide, at least for these particular cases, the nature or mechanism of adsorption over which controversy has ranged so long. To do this, particular attention was paid to the influence of time on the amount of adsorption.

It was found in confirmation of the results of Freundlich that "equilibrium" could be quickly attained from both sides. This must be due to purely surface action. Most striking confirmation of this view, and proof that a second factor comes into play, was obtained by observing the effect of long periods of time. It was found that for weeks, and even months, the carbon continued to adsorb the iodine, and this in relatively large quantities. These two facts can only be explained on the assumption that both surface action and diffusion into the interior of the carbon take place. The surface condensation is nearly instantaneous; the formation of the solid solution is slower and requires weeks or months for its completion.[*]

In the second place, it was desirable to test whether the surface action, as it is supposed by Freundlich, is independent of the nature of the adsorbed and adsorbing substance, other things being equal, or whether, on the contrary, this action is specific. The latter was shown to be the case. For the diffusing part of the adsorbed substance, Henry's law must hold.[†]

EXPERIMENTAL.

Where not otherwise stated, the measurements were carried out as follows.

Carbon was weighed into a 30 c.c. tube, 25 c.c. of a decinormal solution of iodine were added, the tube sealed off and placed in a shaking apparatus in a thermostat. With some of the solvents, the sealing off was done in an atmosphere of nitrogen to avoid ignition. At the conclusion of the experiment, the tube was opened, and about 15 c.c. of the contents were filtered through glass wool, weighed, and titrated with $N/10$-sodium thiosulphate.

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[*] Chemical action might furnish an alternative explanation of the slow after-change, but this hypothesis is entirely excluded on account of the nature of the reagents studied (iodine and carbon). Compare Freundlich, *Habilitationsschrift*, p. 33; Bunsen, *Ann. Phys. Chem.*, 1883, [iii], **20**, 545.

[†] McBain, as yet unpublished.

By using a fresh tube for each experiment and sealing it off after filling, possible errors due to volatilisation, &c., were reduced to a minimum.*

The estimations were performed by shaking with water in a stoppered bottle and titrating directly with sodium thiosulphate, sharp end points being obtained. In the case of alcohol and ethyl acetate, a little potassium iodide was added previously to ensure a correct end-point, starch being used as indicator.

Materials Employed.†—Toluene and benzene were dried by fractionation and rejecting the first portion of the distillate. Chloroform and ethyl acetate were distilled from calcium chloride. For the other experiments, absolute alcohol was employed. The iodine which was dried in a desiccator was made up to decinormal strength, and 25 c.c. were weighed in each case.

Animal carbon, which contains about 90 per cent. of ash, was digested for several days with hot concentrated hydrochloric acid and then washed in running water, and, finally, treated with boiling distilled water until it gave no reactions for phosphates or chlorides; it then contained 1 per cent. of ash.

Kahlbaum's sugar carbon was used, and was found to be free from ash.

1·3 Kilograms of the white endospermic tissue in the cocoanut were shredded and carbonised at as low a temperature as possible in a muffle furnace; 60 grams of charcoal were obtained containing 9·5 per cent of ash.

This was then treated with hydrochloric acid, but the extraction was by no means so effective as in the case of animal carbon, the final product containing 3·9 per cent. of ash. Each variety was dried at 120—130° before use.

Influence of Amount of Carbon.

The following experiments were carried out at 30°. The tables record the duration of the experiment; m the number of grams of carbon taken per 100 c.c., weighed accurately; x/m the number of grams of iodine adsorbed per 1 gram of carbon; $a-x$ the final concentration of the solution, originally decinormal, expressed in grams of iodine per 100 c.c. of solution, and the constants β, p, and λ of the adsorption formula already mentioned.*

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* Compare Schmidt, *Zeitsch. physikal. Chem.*, 1894, **15**, 56, who repeatedly opened his vessels, replacing solution removed for titration by fresh solvent.

† For the very small influence of impurities in the materials, for example, moisture, see Freundlich, *loc. cit.*

$a = 1\cdot2685$ grams of iodine per 100 c.c. original solution.

TABLE I.—*Animal carbon and Toluene.*

$\beta = 0\cdot370$. $p = 3\cdot26$. 24 hours.

m	x/m.	$a-x$.	λ.
2	0·315	0·638	14·9
4	0·253	0·255	17·5
6	0·193	0·110	17·7
8	0·151	0·059	16·6

TABLE II.—*Animal carbon and Benzene.*

$\beta = 0\cdot382$. $p = 3\cdot22$. 3 days.

m.	x/m.	$a-x$.	λ.
2	0·331	0·606	16·0
4	0·249	0·271	16·7
6	0·192	0·117	17·3
8	0·152	0·051	17·5

TABLE III.—*Animal carbon and Ethyl acetate.*

$\beta = 0\cdot430$. $p = 3\cdot26$. 24 hours.

m.	x/m.	$a-x$.	λ.
2	0·357	0·555	17·94
4	0·264	0·211	19·51
6	0·198	0·079	20·13
8	0·154	0·035	19·42

TABLE IV.—*Animal carbon and Alcohol.*

$\beta = 0\cdot466$.* $p = 3\cdot09$.* 24 hours.

m.	x/m.	$a-x$.	λ.
2	0·373	0·522	19·3
4	0·269	0·191	20·5
6	0·199	0·074	20·5
8	0·153	0·039	18·9

* Rejecting fourth measurement.

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* β and p are calculated graphically from the logarithmic diagram $(l_n c, l_n \frac{x}{m})$ see page 1680.

TABLE V.—*Animal carbon and Chloroform.*

$\beta = 0·545$.* $p = 2·98$.* 3 days.

m.	x/m.	$a - x$.	λ.
2	0·412	0·443	22·8
4	0·280	0·145	23·5
6	0·202	0·053	23·0
8	0·154	0·035	19·4

* Rejecting fourth measurement.

TABLE VI.—*Sugar carbon and Toluene.*

$\beta = 0·357$. $p = 2·48$. 24 hours.

m.	x/m.	$a - x$.	λ.
2	0·231	0·806	9·8
4	0·184	0·530	9·5
6	0·141	0·417	8·1
8	0·116	0·334	7·2

TABLE VII.—*Sugar carbon and Benzene.*

$\beta = 0·302$. $p = 2·49$. 4 days.

m.	x/m.	$a - x$.	λ.
2	0·267	0·734	11·9
4	0·214	0·409	12·3
6	0·170	0·243	13·6
8	0·139	0·149	11·6

TABLE VIII.—*Sugar carbon and Ethyl acetate.*

$\beta = 0·315$. $p = 2·87$. 24 hours.

m.	x/m.	$a - x$.	λ.
2	0·280	0·707	12·7
4	0·223	0·372	13·3
6	0·178	0·199	13·4
8	0·145	0·107	13·4

TABLE IX.—*Sugar carbon and Alcohol.**

$\beta = 0·258$. $p = 2·40$. 8 days.

m.	x/m.	$a - x$.	λ.
2	0·234	0·799	10·0
4	0·193	0·494	10·2
6	0·158	0·317	10·0
8	0·133	0·202	9·95

* Temp. 16—17°

TABLE X.—*Sugar carbon and Chloroform.*

$\beta = 0{\cdot}479$.* $p = 5{\cdot}13$.* 4 days.

m.	x/m.	$a - x$.	λ.
2	0·411	0·446	22·7
4	0·296	0·081	29·9
6	0·207	0·024	28·7
8	0·157	0·007	27·8

* Rejecting last two measurements.

The abnormally large exponent p is noteworthy.

TABLE XI.—*Cocoanut carbon and Toluene*; 48 *hours.*

m.	x/m.	$a - x$.	λ.
2	0·025	1·217	0·99
4	0·023	1·173	0·85
6	0·015	1·141	0·76
8	0·017	1·128	0·65

TABLE XII.—*Cocoanut carbon and Ethyl acetate*;* 48 *hours.*

m.	x/m.	$a - x$.	λ.
2	0·006	0·90	0·30
4	0·010	0·87	0·46
6	0·011	0·85	0·52
8	0·008	0·85	0·39

* $a = 0{\cdot}913$.

TABLE XIII.—*Cocoanut carbon and Alcohol*; 48 *hours.*

m.	x/m.	$a - x$.	λ.
2	0·015	1·236	0·54
4	0·015	1·205	0·55
6	0·014	1·179	0·52
8	0·015	1·141	0·59

Influence of Temperature.

In accordance with Freundlich's general experience, it was found that the influence of temperature on the amount of adsorption was quite unimportant. This was further confirmed by the observation that the higher the temperature the smaller became the value of p.

TABLE XIV.—*Animal carbon and Toluene.*

At 0°. $\beta = 0{\cdot}327$. $p = 3{\cdot}80$. 24 hours.

m.	x/m.	$a - x$.	λ.
2	0·293	0·682	13·5
4	0·238	0·314	15·1
6	0·189	0·131	16·4
8	0·151	0·054	17·1

At 30° (compare Table I). $\beta = 0{\cdot}370$. $p = 3{\cdot}26$.

At 60°. $\beta = 0{\cdot}361$. $p = 3{\cdot}23$. 24 hours.

m.	x/m.	$a-x$.	λ.
2	0·319	0·630	15·2
4	0·243	0·294	15·5
6	0·189	0·133	16·3
8	0·151	0·059	16·6

Effect of Time.

TABLE XV.—*Animal carbon and Toluene.**

Time.	Temperature.	x/m.	$a-x$.	λ.
5 minutes	30°	0·229	0·809	9·76
15 ,, ...	,,	0·237	0·793	10·18
30 ,, ...	,,	0·245	0·777	10·64
1 hour	,,	0·265	0·736	11·80
2 hours	,,	0·293	0·682	13·47
5 ,, ...	,,	0·299	0·669	13·88
24 ,, ...	,,	0·315	0·637	14·94
2 days	,,	0·320	0·627	15·27
3 ,, ...	,,	0·329	0·610	15·90
3 ,, ...	(16—18°)	0·313	0·641	14·79
5 ,, ...	30°	0·322	0·622	15·45
5 ,, ...	,,	0·327	0·613	15·76
6 ,, ...	,,	0·338	0·591	16·58
21 ,, ...	16—18°	0·355	0·558	17·83
24 ,, ...	,,	0·379	0·509	19·79

* Two grams of carbon to 100 c.c. of solution.

The original solution had remained unaltered. The final solutions were neutral to methyl-orange, and were not precipitated by silver nitrate after shaking with distilled water.

TABLE XVI.—*Animal carbon and Benzene.** *Temp.* 16—19°.

Time.	x/m.	$a-x$.	λ.
3 days	0·328	0·611	15·9
3 ,, ...	0·331	0·606	16·0
10 ,, ...	0·339	0·589	16·6
26 ,, ...	0·386	0·495	20·4

* Two grams of carbon to 100 c.c. of solution.

The original solution remained unchanged. After shaking the final solution with water, the aqueous solution gave no precipitate with silver nitrate, and was neutral to methyl-orange.

TABLE XVII.*—*Animal carbon and Ethyl acetate.*

Time.	*m*.	*x/m*.	*a − x*.	λ.
15 minutes	2	0·268	0·731	11·95
15 ,, ...	4	0·226	0·363	13·81
15 ,, ...	6	0·181	0·180	14·13
15 ,, ...	8	0·146	0·095	14·06
24 hours	2	0·356	0·555	17·94
3 months †	2	0·429	0·409	21·54

* Compare Table III.

† Laboratory temperature. Placed in thermostat at 30° for last 24 hours.

The iodine strength of the original solution had remained unchanged at the end of the three months.

TABLE XVIII.*—*Animal carbon and Alcohol ; Temp.* 30°.

Time.	*m*.	*x/m*.	*a − x*.	λ.
15 minutes	2	0·302	0·663	14·1
4 hours	2	0·372	0·523	19·2
24 ,, ...	2	0·373	0·522	19·3

* Compare Table IV.

TABLE XIX.*—*Sugar carbon and Toluene ; Temp.* 30°.

Time.	*m*.	*x/m*.	*a − x*.	λ.
2 days	2	0·283	0·701	12·87
,, ...	4	0·228	0·355	13·83
,, ...	6	0·176	0·209	13·04
,, ...	8	0·141	0·139	11·98
3 days	2	0·299	0·669	13·87
,, ...	4	0·235	0·328	14·68
,, ...	6	0·181	0·178	14·18
,, ...	8	0·144	0·109	13·32

* Compare Table VI.

TABLE XX.—*Cocoanut carbon and Toluene.*

$m = 2$; Temp. 30°.

Time.	*x/m*.	*a − x*.	λ.
3 minutes	0·018	1·231	0·64
30 ,, ...	0·036	1·196	1·26
3 hours	0·046	1·175	1·64
3 days	0·062	1·142	2·27
4 ,, ...	0·065	1·137	2·36
1 month*	0·093	1·082	3·46

* Laboratory temperature.

The ash (9·5 per cent.) had not been extracted for these experiments.

TABLE XXI.—*Cocoanut carbon and Alcohol.*

Laboratory temperature. $m = 2$.

Time.	x/m.	$a - x$.	λ.
2 days	0·012	1·243	0·45
2 ,,	0·015	1·236	0·54
9 ,,	0·024	1·220	0·85
64 ,,	0·043	1·180	1·55

As in all the experiments with cocoanut carbon, the titrated solutions were neutral to methyl-orange. The untitrated portions shaken out with water were also neutral to methyl-orange, and gave no precipitate with silver nitrate.

TABLE XXII.—*Cocoanut carbon and Benzene.*

Laboratory temperature. $m = 2$.

Time.	x/m.	$a - x$.	λ.
10 minutes	0·006	1·255	0·22
5 days	0·019	1·229	0·69
19 ,,	0·026	1·216	0·91
51 ,,	0·043	1·182	1·53

TABLE XXIII.—*Cocoanut carbon and Chloroform.*

Laboratory temperature. $m = 2$.

Time.	x/m.	$a - x$.*	λ.
2 days	0·022	1·298	0·75
9 ,,	0·034	1·276	1·14
24 ,,	0·043	1·258	1·45

* $a = 1·3446$

Equilibrium Experiments.

The previous experiments have demonstrated that the bulk of the iodine is adsorbed in the first few minutes. Hence, if a solution containing twice as much iodine (that is, an $N/5$-solution) were used, there would be at once adsorbed an amount of iodine much greater than the total final amount in the first case.

If in the second experiment, after standing in contact with carbon for some time, fresh solvent be added until the total volume of the liquid corresponds to that of an original decinormal iodine solution, it is evident that some of the iodine must be extracted from the carbon. The question then arises, how much will be extracted? Will that amount only be the excess over the final saturation value for long periods of time, or will still more be extracted, so that the carbon will then only contain as much as though it had been in contact with an originally decinormal solution for the same total length of time?

If the adsorption were a purely surface phenomenon, the first would necessarily be the case. If adsorption is exclusively a process of solution, the second could not possibly take place. I have found that the second case actually occurs, thus proving the main thesis of this communication that the adsorption of iodine by carbon is not purely a surface action, nor purely a case of solid solution, complete or incomplete, but a combination of both. The following experiments establish this point.*

In each case, equal amounts of carbon were weighed into two bottles, *A* and *B*, fitted with accurately ground stoppers. Into *A*, 25·0 c.c. of $N/10$-iodine solution were introduced, and simultaneously 12·5 c.c. of $N/5$-iodine solution were added to *B*.

After a certain period, 12·5 c.c. of pure solvent were added to *B*. When the two bottles had stood for twenty-four hours longer, both were opened and a portion of the contents titrated. In all cases, the experiments were carried out at the ordinary temperature.

TABLE XXIV.—*Animal carbon and Toluene.*

Diluted contents of *B* after twenty-four hours, and titrated twenty-four hours later.

	$m.$	$x/m.$	$a-x.$
A.	2	0·304	0·659
B.	2	0·304	0·659
A.	4	0·244	0·291
B.	4	0·244	0·291
A.	6	0·188	0·139
B.	6	0·190	0·126
A.	8	0·150	0·063
B.	8	0·150	0·063

These results at first appear satisfactory, but they are obviously inaccurate, and present the only ground for uncertainty in interpreting the results of the present paper (see p. 1680).

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* Experiments are being carried out with exceedingly finely-divided carbon in order to forestall any such objection as that a relatively long time is necessary for the iodine to finish diffusing (through the liquid) into pores or nearly closed chambers in the carbon. Excessively small chambers can exert no influence, as diffusion here becomes practically instantaneous.

TABLE XXV.—*Animal carbon and Benzene.*

Diluted contents of *B* after twenty-four hours, and titrated twenty-four hours later.

	m.	x/m.	$a-x$.
A. ……………	2	0·338	0·591
B. ……………	2	0·355	0·558
A. ……………	4	0·244	0·291
B. ……………	4	0·250	0·266
A. ……………	6	0·190	0·126
B. ……………	6	0·192	0·114
A. ……………	8	0·148	0·083
B. ……………	8	0·150	0·063

The results in Table XXV are more nearly what might be expected. During the preliminary twenty-four hours, diffusion will be twice as great in *B* as in *A*, and the equalisation of the surface effect in the succeeding twenty-four hours cannot, of course, affect the resulting divergence in "adsorbed" iodine. If the duration of the preliminary exposure be much curtailed, this source of ambiguity in the results will be removed, as is well shown in the following Tables Nos. XXVI, XXVII, and XXVIII.

TABLE XXVI.—*Animal carbon and Benzene.*

Diluted contents of *B* after thirty minutes, and titrated twenty-four hours later.

	m.	x/m.	$a-x$.
A. ……………	2	0·337	0·593
B. ……………	2	0·331	0·605
A. ……………	4	0·247	0·279
B. ……………	4	0·248	0·272

TABLE XXVII.—*Cocoanut carbon and Toluene.*

Diluted contents of *B* after twenty-four hours, and titrated twenty-four hours later.

	m.	x/m.	$a-x$.
A. ……………	2	0·017	1·232
B. ……………	2	0·025	1·217
A. ……………	8	0·009	1·191
B. ……………	8	0·012	1·169

In this case, the contents of *B* were diluted after thirty minutes.

	m.	x/m.	$a-x$.
A. ……………	3	0·012	1·255
B. ……………	3	0·012	1·255

Adsorption in a Vacuum.

The astonishingly small relative adsorption power of cocoanut carbon might possibly be attributed to the very large amounts of air it contains. This, however, is not borne out by the following experiment. The carbon and iodine solution * were placed in the two branches of an inverted U-tube and separated by a glass tap. The branch containing the carbon was then heated in a bath of sulphur vapour, the gases evolved being removed by a Töpler pump. On cooling, the apparatus was sealed off, and the iodine solution allowed to come in contact with the carbon. After twenty-four hours, the following result was obtained:

$$m = 2\,; \quad \frac{x}{m} = 0{\cdot}006\,; \quad a - x = 0{\cdot}90.$$

This is identical with the value in Table XII.

Influence of Solubility.

It is interesting to see how far the relative solubilities of iodine in the various solvents affect the amount of adsorption. It is clear that, on the one hand, there can be no direct connexion with the surface condensation (compare Freundlich, *loc. cit.*), and that, on the other, the amount of diffusion will be proportional to this value (distribution ratio); for iodine has the same molecular formula, namely, I_2, in all the solvents employed (Beckmann, *Zeitsch. physikal. Chem.*, 1895, **17**, 107; 1907, **58**, 543).

To determine the solubilities, tubes containing the various solvents and excess of iodine were shaken for six hours at 8°, and 5 c.c. of the saturated solution were titrated in each case.

TABLE XXVIII.

Solvent.	$N/10$-Sodium thiosulphate required.	Grams of iodine in 100 c.c. of saturated solution.
Alcohol	63·8 c.c.	16·18
Toluene	39·9 ,,	10·12
Ethyl acetate	38·9 ,,	9·87
Benzene	35·2 ,,	8·93
Chloroform	10·6 ,,	2·69

With this may be compared the results obtained for the net adsorption (Tables I to XV).

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* Solution of iodine in ethyl acetate. $a = 0{\cdot}913$.

TABLE XXIX.

Solvent.	λ.		
	Animal carbon.	Sugar carbon.	Cocoanut carbon.
Alcohol	19·8	10·0	0·55
Toluene...............	16·7	8·6	0·8
Ethyl acetate	19·2	13·2	0·42
Benzene..............	16·9	12·3	0·6
Chloroform	23·1	27·1	0·8

The present data are not sufficiently comprehensive for a more thorough analysis of the influence on the two factors, surface action and diffusion.

Discussion of Results.

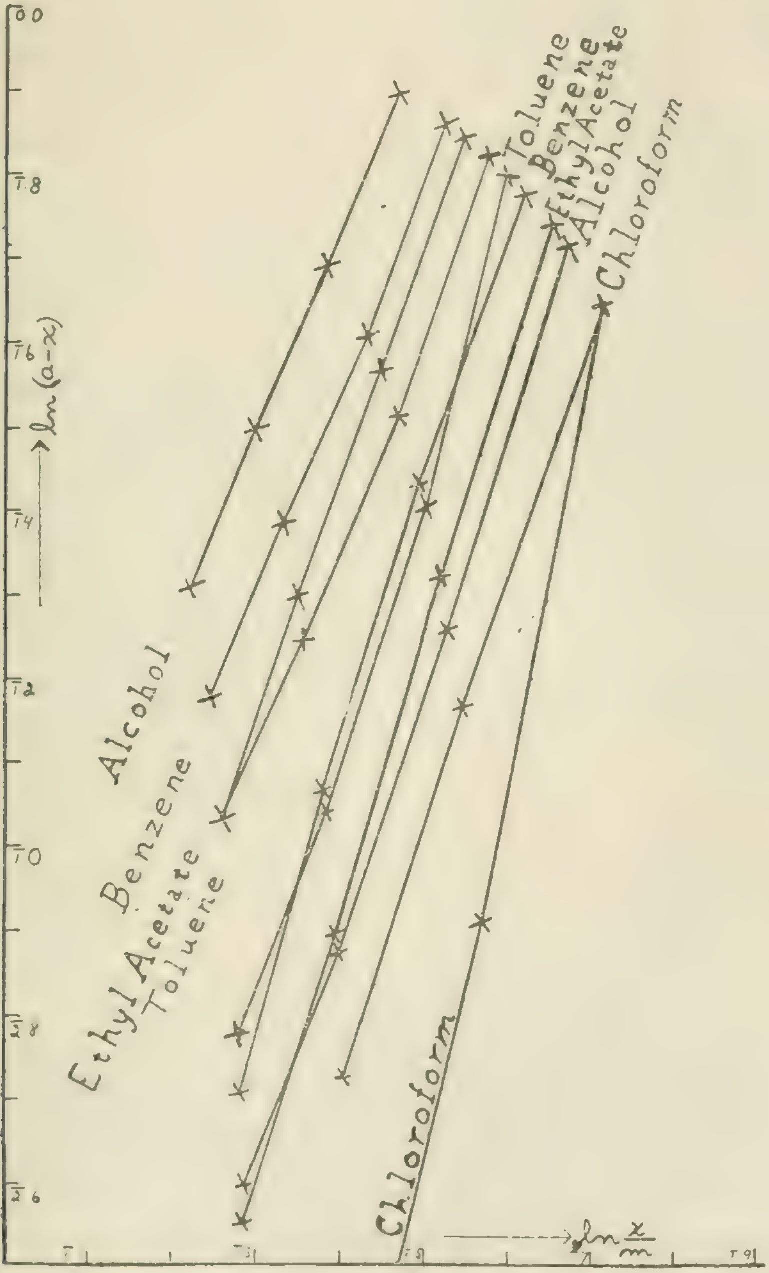
The relationships found are best shown by the graphic representation of the results. The measurements are in excellent agreement with the exponential formula. This formula requires that the results should fall on straight lines in the logarithmic diagram

$$\left(\log \overline{a-x},\ \log \frac{x}{m}\right).$$

The figure presents the results of Tables I—V (animal carbon) and VI—X (sugar carbon), using various solvents at 30° for one or several days. For convenience, the name of the solvent where animal carbon was employed is written at the upper end of the curve, for those experiments with sugar carbon the solvent is indicated underneath.

The simple physical significance of the constants β and $1/p$ in the exponential formula, $\frac{x}{m} = \beta\left(a-x\right)^{\frac{1}{p}}$, is apparent; p is the slope of the straight line and β is the number of grams of iodine per gram of carbon which would be in equilibrium with a solution containing 1 gram of iodine in 100 c.c. Both values are calculated graphically; p is the average of the slopes between the three consecutive pairs of points on each curve, and β is the average distance from the four points of a straight line passing through the origin with this slope; that is, β is the intersection of the straightened curve with the line $\log \overline{a-x} = 0$.

Freundlich has laid down the generalisation that the amount of adsorption is independent of the nature of the adsorbing agent if equal surfaces are compared. The experiments here presented constitute an ideal material with which to test this conclusion. It is not likely that there is great difference in the chemical nature of the carbon when we pass from animal to sugar, or from sugar to cocoanut, charcoal, especially as the amount of adsorption in the first case, and of diffusion in both cases, remain unaffected. Although it is impossible to obtain the various kinds of carbon with identical surface area, yet it is possible to compare the series of experiments with each of the



three varieties of carbon to see whether the change in surface from series to series has produced the same relative effect with each of the solvents. If this be so, the order of the relative adsorption will be the same with each form of carbon. This is found not to be the case, as is evident from the following table.

TABLE XXX.—*Amount of Adsorption* (β).

Animal carbon.		Sugar carbon.		Cocoanut carbon.*	
Toluene	0·370	Alcohol	0·258	Ethyl acetate ...	0·010
Benzene	0·382	Benzene	0·302	Alcohol	0·014
Ethyl acetate ...	0·430	Ethyl acetate ...	0·315	Benzene	0·018
Alcohol	0·466	Toluene	0·357	Chloroform	0·020
Chloroform	0·545	Chloroform	0·479	Toluene	0·021

* Approximate value, calculated through the λ-formula.

These results are decisive, and they are fatal to Freundlich's quantitative generalisation. The variations within the series amount to more than 100 per cent. It is thus established that adsorption is a specific action, dependent on the nature both of the adsorbed and adsorbing material.

Another, although less conclusive method of arriving at the above disproof, is the comparison of the adsorption by animal and cocoanut charcoal. The latter, which is notable for its adsorptive power for gases, does not adsorb a tithe of the amount of iodine that animal or sugar carbon does.

This striking fact cannot be attributed to the possible poorness of the sample of cocoanut carbon employed, for tests made in Travers' apparatus showed it to be as effective as that which he employed.

It is of interest to tabulate the exponential values found. In the case of cocoanut carbon, the adsorption is too small to admit of this calculation.

TABLE XXXI.—*Exponents* (p).

Solvent.	Animal carbon.	Sugar carbon.
Alcohol	3·09	2·40
Toluene	3·26	2·48
Ethyl acetate	3·26	2·87
Benzene	3·22	2·49
Chloroform	2·98	5·13

In conclusion, the following facts may be pointed out. (*a*) The experiments were confined to very dilute solutions, where it can be confidently expected that the maximum of regularity will be found. (*b*) As far as the present somewhat scanty experimental material extends, the after-change (diffusion) has approximately the same value in each case, independent of the kind of carbon.

The work on adsorption is being extended along several lines in this laboratory. I propose to repeat and amplify the experiments recorded in this paper in the hope of obtaining exact data for the separate study of the two factors which I have shown play an almost equal part in the phenomenon of adsorption; this will require at least a year, and hence these measurements are communicated now as being sufficient to establish the two main theses of this paper.

SUMMARY.

1. The adsorption of iodine by various charcoals has been definitely proved to consist of a surface condensation and a diffusion (solid solution) into the interior of the carbon.

2. The surface condensation is nearly instantaneous, and is quite complete in some hours; the diffusion proceeds for weeks or months.

3. The independent nature of the surface condensation factor is shown by the fact that in short time experiments the same equilibrium point is attained by starting from both sides. This equilibrium point lies far below the amount of adsorption which results from longer contact with either the dilute or concentrated solution.

4. For sugar and animal carbons, the amount of adsorption is, roughly, the same, the surface condensation being more prominent. Cocoanut carbon adsorbs only a small percentage of this amount, and that chiefly owing to diffusion into the interior.

5. The amount of adsorption is not independent of the nature of the adsorbing surface for identical surface area, but is specific, depending both on the nature of the solvent and the adsorbing solvent.

In conclusion, my thanks are due to my colleague, Mr. James W. McBain, for the interest he has taken in the work, and for assistance in preparing it for publication.

UNIVERSITY COLLEGE, BRISTOL.

CLIX.—*Adsorption Formulae.*

By JAMES W. McBAIN.

QUITE recently Freundlich published a monograph (*Habilitationsschrift*, Leipzig, 1906; *Zeitsch. physikal. Chem.*, 1907, **57**, 385; also Freundlich and Losev, *Zeitsch. physikal. Chem.*, 1907, **59**, 284) on adsorption which, from its comprehensiveness, both on the experimental and on the theoretical side, seems likely to exert the greatest influence on the subsequent development of the subject. He has chosen to express his results partly by means of the well-known exponential formula, but mainly by employing an extension of an expression proposed in an old dissertation by Kreeker (*Dissertation*, Berlin, 1892). The object of the present paper is to point out some very serious disadvantages inherent in the use of this λ-formula.

The exponential and the λ-formulæ are the following:

$$\frac{x}{m} = \beta c^{\frac{1}{p}} = \beta\left(\frac{a-x}{v}\right)^{\frac{1}{p}}$$

$$\lambda = \frac{v}{m} ln \frac{a}{a-x} = \alpha\left(\frac{a}{v}\right)^{-\frac{1}{n}};$$

x is the amount of substance adsorbed; a is the total amount of that substance; $\frac{a-x}{v} = c$ is therefore its concentration in the fluid phrase; m is the weight of adsorbing substance and λ, β, α, p, and n are constants. The formulæ are applicable to gases or solution.

Freundlich has pointed out that for solutions, neither of these is the ultimate complete formula covering all concentrations, for both are based on the apparent adsorption—the decrease in concentration—of only the one substance, generally the solute. Now, in general, if the proportions of the components of the solution be reversed, so that what was previously solvent is now present only in dilute solution, not only the amount, but even the sign, of the adsorption as before calculated will be changed. Hence I shall limit the exposition of the λ-formula to the fewest possible words.*

Unlike as the two expressions appear, Freundlich, by expanding them into infinite series and then neglecting all but the first term, showed that they are not wholly unrelated. Apparently then $\alpha = \beta$ and $\frac{1}{p} = 1 - \frac{1}{n}$. A rigorous analytical and graphical treatment has shown, however, that this is not the case, as will be seen.

If $ln\frac{x}{m}$ and lnc are plotted, the exponential formula is represented by a straight line, p being its tangent or slope. The experimental data, in general, agree fairly well with this, the values of p lying between 2 and 4. If the curves representing constant values of λ be plotted on this same diagram, a being held constant, instead of straight lines, we get the system of parallel curves represented by the figure. It will be seen that the slope has all values between 0 and ∞. The curves are asymptotic at the horizontal line representing a.

If the value of a, the original concentration, is changed, the system is moved bodily at an angle of 45°; upwards and to the right for an increase, downwards to the left for a decrease. The curves remain unaltered in form and relative position. Their form is the same for all substances under all conditions.

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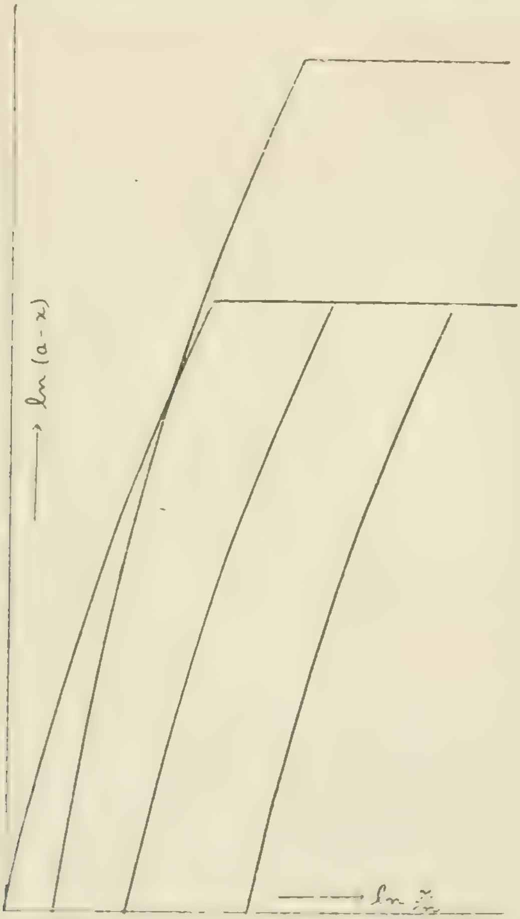
* It should be possible to obtain at least the approximate values for the real adsorption, as distinguished from the apparent adsorption, by studying the adsorption values found in a mixture in which the components are varied all the way from 0 to 100 per cent.

The slope of these curves is dependent only upon initial (a) and final (c) concentrations in the fluid phase. It is:

$$\frac{dlnc}{dln\frac{x}{m}} = \frac{(a-c)ln\frac{a}{c}}{(a-c)-cln\frac{a}{c}}.$$

The following table gives representative values for the parts of the curve between the extreme limits at all likely to occur in practice. The values are quite independent of the units employed; c and x are conveniently indicated in per cent. of a, the total original amount, which is thus tacitly assumed to be equal to 100.



Amount adsorbed. c per cent.	Final concentration. x per cent.	Slope, $\frac{dlnc}{dlnx/m}$.
0·01	99·99	0·129
0·1	99·9	1·904
1	99	2·014
10	90	2·043
20	80	2·073
50	50	2·260
90	10	3·093
99	1	4·831
99·9	0·1	6·972
99·99	0·01	9·221

It will be seen that an apparent agreement with the exponential formula (constant slope) will be obtained only where the equilibrium values are varied between very narrow limits (a change in a if compensated by an equivalent change in the amount of solid employed does not constitute a variation of the equilibrium values). The λ-values on our logarithmic diagram are concave towards the right. Davis's results (see the preceding paper) and even those of Freundlich (tables II—XI, with the exception of Table VI, which are all that I have examined) show no tendency to this. Indeed, from the considerations adduced in the third paragraph above, one could predict, at least for the higher portions of the lines, a curvature to the left.

In the λ-formula, $\lambda = a\left(\frac{a}{v}\right)^{-\frac{1}{n}}$, the slope is not equal to $1 - \frac{1}{p}$, but it is exactly equal to $1 - 1/$slope of the respective λ-curves passing through that particular point on the $\left(ln\frac{x}{m}, lnc\right)$ diagram. Hence it is not a constant and may assume all values between $+1$ and $-\infty$. Fortunately for the formula, these inconvenient manifestations, like some of the others noted, occur in regions not easily susceptible of exact measurement (c or $a - c$ too small in proportion to a).

Consider a concrete case, taking a definite point on the logarithmic diagram. Suppose a decinormal solution in equilibrium with a solid which has adsorbed 0·0001 gram-molecule of solute per gram. The value of λ for this self-same equilibrium may be any number whatsoever, depending on the volume of solution taken and its initial concentration, quite apart from whether the substance is much or little adsorbed.

If 100 c.c. of the decinormal solution were in equilibrium with 1 gram of adsorbing substance, and then 90 c.c. were decanted off, the exponential formula demands that the concentration of the remaining 10 c.c. be unaltered. The λ-formula is mute on the subject. Assuming that it is not altered, we can calculate the new value which λ assumes. But if the equilibrium be unaffected in this one case, the λ-formula predicts that it must be affected in every other case. This is the point I wish to emphasise.

This is best seen graphically; when 90 c.c. of the decinormal solution were poured off, a and hence λ was changed. But this new λ-curve which now runs through our point on $(ln\frac{x}{m}, lnc)$ the diagram came up from below on the left. Hence its slope at this point is steeper than before, and it does not coincide above and below with the λ-curve previously there (see upper curve on diagram). These continuations above and below, however, represent the series of equilibria predicted for constant a and λ. As is evident, the predictions are widely at variance and irreconcilable. In the field covered by Davis's experiments, for example, this could have meant a divergence greater than the total amount of adsorption.*

Thus it is seen that if one equilibrium point be determined, we may, by starting from a different original concentration and varying the amount of adsorbing solid accordingly, predict almost any desired amount of adsorption whatever, per gram, to be in equilibrium with any one fixed concentration of solution. On the other hand, if two equilibria (two points on the diagram) be known, λ and a become fixed, and we arrive at the mathematical prediction that there is only one original concentration from which these two equilibria may be realised, which likewise is more than unlikely.

To sum up: the system of λ-formulæ introduced recently by Freundlich to represent the amount of adsorption does not lead to any definite number characteristic of each set of substances, and, further, its results are irreconcilable with each other and with experiment.†

University College, Bristol.

CLX.—*The Formation and Reactions of Imino-compounds. Part V. The Formation of Methyl Derivatives of* 1:3-*Naphthylenediamine from the Three Tolylacetonitriles.*

By Ernest Francis Joseph Atkinson and Jocelyn Field Thorpe.

In Part II of this series (Trans., 1906, **89**, 1906) it was shown that ethyl β-imino-α-cyano γ-phenylbutyrate (I), which was formed by the condensation of phenylacetonitrile with the sodium compound of ethyl cyanoacetate, passed on treatment with cold concentrated sulphuric acid into ethyl 1 : 3-naphthylenediamine-2-carboxylate (II), from which 1 : 3-naphthylenediamine (III) could be prepared by hydrolysis and elimination of carbon dioxide :

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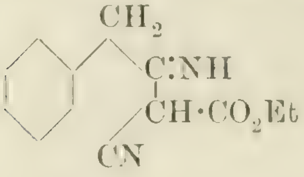
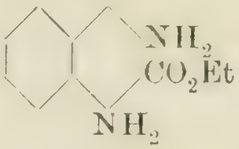
* He avoided this by keeping a constant throughout.

† The above paper was submitted to Dr. Freundlich as it stands and is published with his approval. In a very courteous letter he states that he has increasingly felt it a great weakness in the λ-formula that an equilibrium should thus be referred to a parameter a/r with which it has no apparent connexion; so much so that in his most recent paper ("Über Kolloidfällung und Adsorption," *Zeitsch. Chem. Ind. Kolloide*, 1907, **1**, 321) he has employed only the exponential formula.

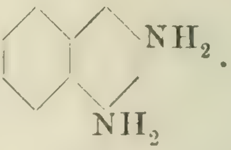
In regard to the question as to whether there is anything behind the fact that the λ-formula can actually be used to represent a large number of cases of adsorption, Freundlich shows that a connexion between dynamic and static surface tension would necessitate some such relation. It is probably well to remember, however, that there is an infinite number of systems of real curves which may be plotted upon the logarithmic diagram; should any of these run by chance obliquely up and down for at least a part of its course with a slope of about 3, and should it further have a simple formula, it could be employed as an adsorption formula.



I.



II.



III.

In the present research, in order to prove the applicability of this reaction to other imino-nitriles and also with the hope of throwing some light on the remarkable colour change which always accompanies it, we have investigated the behaviour of derivatives of ethyl β-imino-α-cyano-γ-phenylbutyrate containing a methyl group in the ortho-, meta-, and para-positions respectively, towards concentrated sulphuric acid, and for this purpose have condensed the three tolylacetonitriles with the sodium derivative of ethyl cyanoacetate, and have investigated the products.

The formation of the three tolylacetonitriles was effected in the usual way by treating the corresponding bromides in alcoholic solution with potassium cyanide, but unexpected difficulties were encountered in ascertaining the best conditions for the formation of the three ω-bromoxylenes.

The present research was carried out conjointly with another which has for its object the investigation of the conditions of formation of derivatives of anthracene and phenanthrene from the three ωω′-dibromoxylenes, and since in that research, an account of which will be shortly placed before the Society, considerable quantities of the three dibromoxylenes were required, the opportunity was taken of investigating the behaviour of the three xylenes on mono- and dibromination under different conditions at 130°.

The chief difficulties arose, not so much in preparing the bromo-derivatives in a pure condition, as in obtaining them in sufficiently large yields for the purposes of the researches. With *m*-xylene the small yield, although troublesome, did not so much matter, since this hydrocarbon can be obtained comparatively cheaply, but with the more expensive *o*- and *p*-xylenes it was a matter of considerable importance to ascertain the correct conditions for the formation of the mono- and di-bromo-derivatives ; moreover, it seemed to us of interest to investigate the nature of the by-products to the formation of which the poor yield was due.

We find that with all three xylenes there is a marked tendency both on monobromination and on dibromination at 130° to form higher brominated products, and this tendency is most marked with the meta- and para-hydrocarbons and least with *o*-xylene. Thus when the three hydrocarbons are monobrominated, although the products consist for the most part of the monobromo-derivatives, yet there is always present a considerable quantity of unchanged hydrocarbon and a corresponding quantity of dibromo-derivative.

In this respect *m*- and *p*-xylene behave in much the same way, but the ortho-hydrocarbon gives a greater quantity of the monobromo-derivative and only a small amount of the unchanged hydrocarbon and dibromo-derivative. So large was the quantity of unchanged hydrocarbon in the case of both *m*- and *p*-xylene that in the monobromination of these hydrocarbons an excess of bromine corresponding with this amount of unchanged hydrocarbon (which had been previously found by experiment) was always added. The separation of the three products formed from each hydrocarbon can then be readily effected by fractional distillation under the ordinary pressure.

The behaviour of the three xylenes on dibromination is closely analogous to their behaviour on monobromination, and the products in the case of the meta- and para-hydrocarbons consist of about equal proportions of mono-, di-, and tri-bromo-derivatives. Here again, however, the ortho-hydrocarbon gives the greatest yield of the dibromo-derivative and only small quantities of the mono- and tri-brominated compounds. The separation of the products in this case is therefore easy, but with *m*- and *p*-xylene the formation of large quantities of the tribromo-compound renders complete separation either by recrystallisation or by distillation a long and tedious process. Thus the separation of the three products from the dibromination of *p*-xylene can only be effected by an exhaustive process of fractional recrystallisation, whilst in the case of *m*-xylene, although a quantity of pure dibromo-compound separates from the product of bromination on standing, yet the mother liquors have to be repeatedly fractionated under diminished pressure before separation is complete.

The large proportion of higher brominated products formed in these reactions seemed to suggest that the method of adding the bromine to the boiling hydrocarbon might have some influence on the result, and in order to test this point a number of experiments were carried out in which the halogen was added in different ways. The method employed by Radziszewski and Wispek (*Ber.*, 1882, **15**, 1743), W. Löw (*Annalen*, 1885, **231**, 363), and Pellegrin (*Rec. trav. chim.*, 1899, **18**, 458), in which the vapour of the halogen was allowed to react with the boiling hydrocarbons, was not found satisfactory owing to the difficulty experienced in preventing the hydrogen bromide formed from carrying away with it some of the bromine vapour. After numerous experiments the following apparatus was devised by which the behaviour of the hydrocarbons under two distinct sets of conditions could be studied. A litre Geissler flask with a ground-in air condenser was fitted with a dropping funnel which was fused into the neck of the flask. In the first set of experiments the delivery tube of the dropping funnel was carried to the bottom of the flask so that the bromine entered at the lowest possible point in the liquid contained in the flask. The three xylenes were then brominated and dibrominated at 130° and the products investigated. In the second set of experiments the delivery tube of the dropping funnel was broken off, by means of a hot wire, about 3 cm. from its further end, under which conditions the tube just dipped below the surface of 150 grams of the hydrocarbon contained in the flask. The products formed from the three hydrocarbons on mono- and di-bromination under these conditions did not differ from those formed under the first set of conditions, which seems to show that the actual method of adding the bromine has no effect on the proportions of the various products formed on the reaction.

During the course of these experiments we have isolated considerable quantities of the ω-tribromo-derivatives of *o*-, *m*-, and *p*-xylene. The first two do not appear to have been described before, and we intend shortly to publish an account of these compounds, and also of the aldehyde-alcohols derived from them on treatment with potassium carbonate. The ω-tribromo-derivative of *p*-xylene has been prepared by W. Löw (*Annalen*, 1885, **231**, 363), who gives its melting point at 106°, and by Allain (*Bull. Soc. chim.*, 1894, [iii], **11**, 382), who describes it as melting at 116° with decomposition. The compound prepared by us melts at 106° without decomposition, in accordance with the observation of Löw.

The ω-dibromoxylene which is prepared in by far the largest yield is the ortho-compound which, as mentioned by Perkin (Trans., 1888, **53**, 5), is formed to the extent of 73 per cent. of the theoretical by the direct dibromination of the hot hydrocarbon. Kipping (Trans., 1888, **53**, 26) prepared the ω-dibromo-derivatives of both *m*- and *p*-xylene, and remarks that the meta-compound is formed in comparatively small amount. The para-compound is, however, produced, he says, to the extent of 85—90 per cent. of the theoretical. We have unfortunately never been able to prepare this substance in greater yields than 40 per cent., for although the product of dibromination completely solidified on cooling, yet on examination it was found to consist of about equal proportions of monobromo-, dibromo-, and tribromo-*p*-xylene.

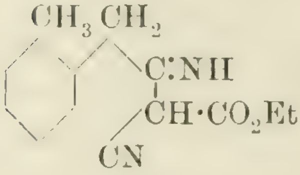
When preparing ω-dibromo-*m*- and *p*-xylene, we have always found it more advantageous to recover them as by-products in the preparation of the monobromo-derivative than to prepare them by the direct dibromination of the hydrocarbons. As already mentioned, excess of bromine is always employed in preparing the monobromo-derivatives of these two hydrocarbons, and the products therefore consist of the monobromo- and dibromo-derivatives which can be readily separated by fractional distillation. When once the tribromo-derivatives of these hydrocarbons are formed in any quantity, the separation of the dibromo-compounds in a pure condition appears to be a long and tedious process.

The conversion of the mono- and di-bromoxylenes into the corresponding nitriles and dinitriles presented few difficulties, and was carried out in accordance with the methods of previous investigators. It was noticed, however, as regards the ω-dibromoxylenes that the reaction with potassium cyanide in alcoholic solution proceeded in the case of the ortho-compound with very much greater readiness than with the meta- or para-derivatives. In fact, if the heating of ω-dibromo-*o*-xylene with alcoholic potassium cyanide is continued longer than three hours hardly any of the dinitrile can be isolated, but the product consists of a crystalline substance isomeric with the dinitrile, which possesses rather remarkable properties.

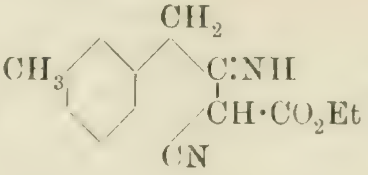
The same compound is also formed when the pure dinitrile is heated with sodium ethoxide, and its preparation and properties will therefore be dealt with in a later paper on the formation of derivatives of anthracene and phenanthrene from the phenylenediacetonitriles. One curious property of *o*-phenylenediacetonitrile, which does not appear to have been previously noticed, may, however, be recorded here. The dinitrile crystallises well from methyl alcohol at the ordinary temperature in large, colourless prisms melting at 59—60°. If, however, the methyl-alcoholic solution is cooled below 18°, the compound crystallises in long, flat needles, which, after a few seconds, pass into the prismatic form, the change being accompanied by a comparatively loud detonation.

In studying the formation of the naphthalene ring from imino-derivatives of the three xylenes containing the requisite side-chain, the compounds investigated in each case were the condensation products of the three mononitriles with the sodium compound of ethyl cyanoacetate.

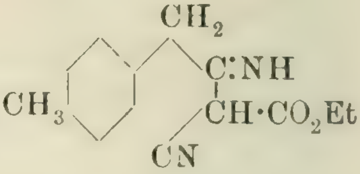
It was found that in each case a good yield of the condensation product was obtained in these reactions, and, moreover, since the whole of the mononitrile which had not entered into the reaction could be completely recovered by distilling the product in steam, it was possible by repeating the process three times to convert the whole of the mononitrile into the imino-nitrile. The constitution of each of these condensation products was determined in the usual way by alkaline hydrolysis when the formation of *o*-tolylacetic acid, *m*-tolylacetic acid, and *p*-tolylacetic acid from the three products respectively showed that they were the ortho-, meta-, and para-forms of ethyl β-imino-α-cyano-γ-tolylbutyrate, and possessed formulæ represented by (IV), (V), and (VI).



IV.

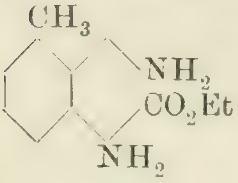


V.

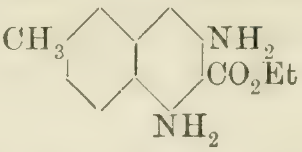


VI.

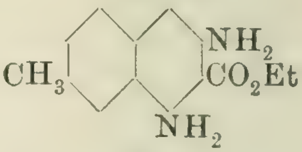
When treated with cold concentrated sulphuric acid these three isomeric forms of ethyl β-imino-α-cyano-γ-tolylbutyrate are immediately converted into the corresponding methyl derivatives of ethyl 1 : 3-naphthylenediamine-2-carboxylate (VII), (VIII), and (IX).



VII.

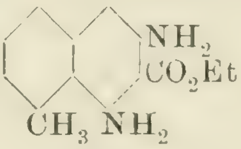


VIII.

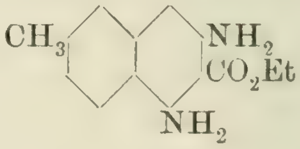


IX.

A close study of the formulæ (IV), (V), and (VI) shows, however, that whereas the ortho-derivative (IV) has only one free ortho-position in respect to the side-chain and can therefore give only a compound of formula (VII) on ring formation, the meta- and para-compounds (V) and (VI) both have two ortho-positions with which ring formation can take place. With the para-compound the two ortho-positions are identical and therefore the only compound which can be formed is that represented by formula (IX) in which ring formation has taken place in the meta-position with respect to the methyl group. With the meta-compound, however, the two positions are different and ring formation can take place either in the ortho-position with respect to the methyl group or in the para-position to this group. The compound formed from the meta-derivative can therefore have either of the formulæ (X) or (XI).

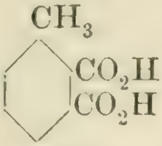


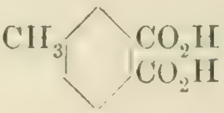
X.



XI.

The only way to establish the formula of the compound formed from ethyl-β-imino-α-cyano-γ-*m*-tolylbutyrate was to oxidise it to the corresponding methylphthalic acid. Monnet, Reverdin and Noelting (*Ber.*, 1879, **12**, 2306) have shown that α-naphthylamine yields phthalic acid on oxidation with chromic acid, and if, as was to be expected, the derivative of 1 : 3-naphthylenediamine derived from the meta-compound behaved in the same way the constitution of the base of either formula (X) or (XI) could be determined by the identity of the methylphthalic acid formed from it on oxidation. Thus the two methylphthalic acids would be (XII) and (XIII).

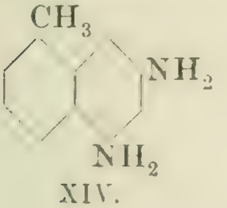

XII.

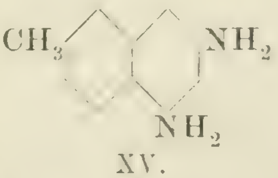

XIII.

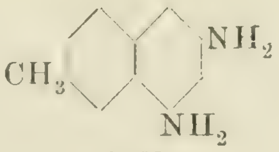
Both these acids are known, the compound of formula (XII) having been prepared by Young (*Ber.*, 1892, **25**, 2108), who found it to melt at 144° and to give an anhydride melting at 109—110°, whilst the acid of formula (XIII) has been investigated by both Young (*loc. cit.*, 2108) and Niementowski (*Monatsh.*, 1891, **12**, 624), who find it to melt at 152° and to yield an anhydride melting at 92°.

The base derived from ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate was oxidised according to the directions of Monnet, Reverdin, and Noelting for α-naphthylamine and a small quantity of an acid of the formula $C_9H_8O_4$ was obtained which melted at 152° and gave an anhydride melting at 92°. It is therefore evident that ring formations in the case of the meta-compound takes place in the para-position with respect to the methyl group and that the formula of the naphthalene derivative is that represented by (XI).

The ethyl salts of the alkyl-1 : 3-naphthylenediamine-2-carboxylic acids are converted on hydrolysis into the corresponding carboxylic acids which readily lose carbon dioxide and pass into the three methyl-1 : 3-naphthylenediamines (XIV), (XV) and (XVI).


XIV.


XV.


XVI.

It was stated in Part II (p. 1911) that ethyl β-imino-α-cyano-γ-phenylbutyrate when dissolved in concentrated sulphuric acid at the ordinary temperature formed a deep malachite green solution which became colourless on dilution with water, giving a solution of the sulphate of ethyl 1 : 3-naphthylenediamine-2-carboxylate. It was also mentioned that if the solution in concentrated sulphuric acid was effected at 0° the green solution was not formed, but that the yield of the naphthalene derivative was in each case practically the same. The formation of similar green solutions was noticed in the transformation of ethyl β-imino-α-cyano-γ-phenylvalerate into ethyl methyl-2 : 4-naphthylenediamine-3-carboxylate (Trans., 1906, **89**, 1924), ethyl *β*-imino-*α*-cyano-*γ*-phenyl-*n*-hexoate into ethyl 1-ethyl-2 : 4-naphthylenediamine-3-carboxylate (*loc. cit.*, p. 1928), ethyl *β*-imino-*α*-cyano-*γ*-*o*-tolylpropionate into ethyl 1 : 3-naphthylenediamine-2-carboxylate (Trans., 1907, **91**, 587), and ethyl *γ*-imino-*α*-cyano-*γ*-phenylbutyrate into ethyl 1 : 4-naphthylenediamine-3-carboxylate (Trans., 1907, **91**, 1008); in every case the colour was not formed when the solution in sulphuric acid was effected at 0°, and since the naphthalene derivatives produced in the reactions did not themselves give any colour with sulphuric acid it was apparent that the formation of the colour must have been due to the presence in small quantities of some other substances which were formed at the ordinary temperature but not at 0°. A study of the compounds described in the present paper has enabled us to ascertain the cause of this colour and to isolate the compounds to which its formation is due.

The colour changes which ensue when the three isomeric ethyl *β*-imino-*α*-cyano-*γ*-tolylbutyrates are dissolved in concentrated sulphuric acid at the ordinary temperature are very characteristic and readily serve to distinguish these compounds the one from the other.

Ethyl-*β*-imino-*α*-cyano-*γ*-*o*-tolylbutyrate (IV) dissolves, forming an intense brown-red solution, which on dilution with water becomes first olive-green and finally, on further dilution, pale yellow.

Ethyl *β*-imino-*α*-cyano-*γ* *m*-tolylbutyrate (V) dissolves, forming a cherry red solution, which on dilution becomes at once practically colourless without other change.

Ethyl *β*-imino-*α*-cyano-*γ*-*p*-tolylbutyrate (VI) dissolves, forming an intense magenta-red solution which on dilution becomes first violet, then blue, then green, and finally pale yellow.

The colours produced in the case of the ortho- and para-derivatives are very much more intense than those formed in any of the other cases investigated, and it was at once apparent that the colour-forming constituents were produced in these reactions to a very much greater extent than in any of the others. It was hardly surprising, therefore, to find that the products of the action of sulphuric acid on the ortho- and para-compounds at the ordinary temperature contained only small quantities of the corresponding naphthalene derivatives, but that they each consisted of a phenolic base which, when dissolved in concentrated sulphuric acid, gave the characteristic colour of the reaction in which it was formed. A complete investigation of these compounds is in progress.

The meta-derivative, which dissolves in sulphuric acid giving a colour much less intense than that formed by the other two and which is not formed at all at −5°, gives hardly any of this phenolic basic substance, and in this case, as in those previously investigated, the yield of the naphthalene derivative is practically quantitative, it being immaterial whether the reaction is carried out at 0° or at the ordinary temperature. In the case of the ortho- and para-derivatives, however, it is impossible to prevent the formation of the colour, even when the reaction is carried out at −10°, and although at the lower temperature the yields of the naphthalene derivatives are slightly increased yet they never exceed 10 per cent. of the theoretical amount.

Although it would be premature to speculate as to the causes of this remarkable difference in behaviour until the identity of the phenolic bases to which reference has been made has been established, yet it is worthy of remark that both the ortho- and para-derivatives are alike in this respect, namely, that ring formation in each of them has to take place in the meta-position with respect to the methyl-group. It would therefore appear at first sight as if the meta-position of the methyl group exercised a marked inhibiting effect on the formation of the naphthalene ring. It is hoped that further work will throw light on this point.

EXPERIMENTAL.

Bromination of o-*Xylene.*

Since it was established by experiment that the method of adding the bromine to the hot hydrocarbon had little effect on the nature of the product, the same apparatus was used throughout in the bromination of the three xylenes. The bromine was allowed to enter very slowly below the surface of the hydrocarbon contained in a Geissler flask heated to 130° in an oil-bath.

Monobromination.—It has been mentioned in the introduction that preliminary experiments had shown that the monobromination of all three xylenes yielded varying quantities of unchanged hydrocarbon and a corresponding amount of ω-dibromo-derivative, and that the method was therefore adopted of adding an excess of bromine corresponding with this amount of unchanged hydrocarbon in order that the greatest yield of the monobromo-derivative might be obtained. In the case of *o*-xylene the quantity of hydrocarbon recovered unchanged from 150 grams was only 15 grams and therefore the quantity of bromine used in subsequent experiments was 252 grams. When all the bromine had been added the product was poured into an evaporating basin and placed in an evacuated desiccator over potash until free from hydrogen bromide, when it was transferred to a distillation flask and distilled at the ordinary pressure. The fraction distilling at 215—218° was collected and used directly for conversion into the nitrile. The yield was 80 per cent. of the theoretical, the small quantity of dibromo-compound formed in the reaction remaining in the distillation flask, in which it solidified on cooling.

Dibromination.—The ortho-derivative was the only one of the three xylenes in the dibromination of which the direct action of four atoms of bromine on the hydrocarbon is to be recommended for the production of the dibromo-derivative in large quantities. The quantities employed were those recommended by Perkin (Trans., 1888, **53**, 5), the product being washed with chloroform and recrystallised from this solvent. We obtained a yield of the pure product corresponding with 73 per cent. of the theoretical, being the same as that obtained by Perkin.

ωωω'-Tribromo-o-xylene, $CHBr_2{\cdot}C_6H_4{\cdot}CH_2Br$.—This substance was recovered from the chloroform mother-liquors and washings from the above dibromination. The chloroform was evaporated on the water-bath and the remaining semi-solid mass was washed with cold light petroleum (b. p. 80—90°). The solid residue, after being recrystallised three times from light petroleum, was obtained in colourless, glistening plates melting at 97°:

0·4021 gave 0·6592 AgBr. Br = 66·92.

$C_8H_7Br_3$ requires Br = 70·0 per cent.

The substance is converted on boiling with a solution of potassium carbonate into the corresponding aldehyde-alcohol.

Bromination of m-*Xylene.*

Monobromination.—The quantity of *m*-xylene recovered from 150 grams of the hydrocarbon on treatment with two atomic proportions of bromine being 50 grams, the amount of bromine taken in subsequent experiments with the same quantity of *m*-xylene was 302 grams. The bromination was carried out in the usual way and the product, after being freed from hydrogen bromide, was distilled under the ordinary pressure. The fraction distilling at 212—215° was collected, the yield being 47 per cent. of the theoretical. The residue in the flask, which consisted of the dibromo-compound, was washed with a little light petroleum (b. p. 80—90°) and then recrystallised from this solvent, when the pure dibromo-derivative was obtained in a yield of 45 per cent. of the theoretical.

Dibromination.—As already mentioned the preparation of ω-dibromo-*m*-xylene by the direct bromination of *m*-xylene with four atomic proportions of bromine was abandoned owing to the difficulty experienced in separating the mixture of mono-, di-, and tri-bromo-derivatives formed. One experiment was, however, carried out in order to investigate the products formed in the reaction.

One hundred and fifty grams of the hydrocarbon were treated with

460 grams of bromine in the manner already described and the product, after being freed from hydrogen bromide in an evacuated desiccator over potash, was allowed to stand for two days. At the end of this time a quantity of crystals had separated. These were collected and washed with a little light petroleum (b. p. 80—90°), when they proved to be the pure dibromo-derivative, the quantity formed representing 23 per cent. of the theoretical. The light petroleum washings were then evaporated to dryness, the residue mixed with the mother-liquors from the crystals, and the whole carefully fractionated three times under a pressure of 18 mm.

In this way three chief fractions were obtained: (*A*) 140—150°, the greater quantity boiling constantly at 145°; (*B*) 160—170°, a small fraction of which the greater portion boiled constantly at 163°; and (*C*) 180—190°, boiling almost constantly at 184°.

Fraction (*A*) consisted of almost pure monobromo-derivative and on distillation under the ordinary pressure boiled at 212—214°, the yield being 28 per cent. of the theoretical. Fraction (*B*) solidified on standing and the solid on washing with light petroleum yielded pure ω-dibromo-*m*-xylene, the quantity obtained added to that already isolated bringing the yield up to 30 per cent. Fraction (*C*) also completely solidified on standing. It was dried on a porous plate and crystallised from light petroleum (b. p. 90—110°), being obtained in large prisms melting at 118°.

0·4154 gave 0·6824 AgBr. Br = 69·90.

$C_8H_7Br_3$ requires Br = 70·0 per cent.

This substance is therefore *ωωω'-tribromo-*m*-xylene*,

$$CHBr_2{\cdot}C_6H_4{\cdot}CH_2Br,$$

and the quantity formed represented 29 per cent. of the theoretical. On boiling with potassium carbonate solution the tribromo-derivative is converted into the corresponding aldehyde-alcohol.

It is therefore evident that under the experimental conditions described the dibromination of *m*-xylene at 150° leads to the formation of about equal quantities of monobromo-, dibromo-, and tribromo-derivatives.

Bromination of p-*Xylene.*

Monobromination.—The quantity of unchanged *p*-xylene recovered from the bromination of 150 grams of the hydrocarbon with two atomic proportions of bromine was found to be 45 grams and therefore in subsequent experiments the quantity of bromine used for the bromination of this weight of hydrocarbon was 294 grams. The product of bromination, after being freed from hydrogen bromide, was distilled twice under the ordinary pressure, yielding two chief fractions (*A*) 210—220° and (*B*) 240—250°. Both fractions solidified on cooling. Fraction (*A*), the greater portion of which boiled constantly at 212°, crystallised in long needles melting at 35·5°, evidently therefore consisting of the pure monobromo-derivative. The quantity formed represented 46 per cent. of the theoretical. Fraction (*B*), which boiled practically constantly at 245°, was crystallised from benzene, when a quantity of the large characteristic prisms of ω-dibromo-*p*-xylene melting at 143·5° separated. The amount corresponded with 48 per cent. of the theoretical.

Dibromination.—Under the experimental conditions used by us the dibromination of *p*-xylene follows a course very similar to that of the meta-hydrocarbon and leads to the formation of about equal quantities of mono-, di-, and tribromo-derivatives. The bromination was effected with 150 grams of the hydrocarbon and 460 grams of bromine, the product being poured into an evaporating basin, in which it instantly solidified. The crude solid which melted between 110—120° was first ground with cold light petroleum (b. p. 80—90°), whereby the whole of the monobromo-derivative passed into solution. The solid residue was then boiled with a little light petroleum, in which solvent the dibromo-derivative is insoluble, whereas the tribromo-derivative dissolves. The solid, which was filtered from the hot light petroleum solution, therefore consisted of the pure dibromo-derivative and this was finally crystallised from benzene. The hot light petroleum filtrate on cooling deposited the tribromo-derivative mixed with a little dibromo-compound and the tribromo-derivative was ultimately obtained pure by repeating this process. The petroleum mother-liquors from all the fractions were then evaporated to dryness and the residue again rubbed with cold petroleum, the insoluble portion being worked up as before. In this way the di- and tri-bromo-derivatives were completely separated and the monobromo-compound was recovered on evaporating the final petroleum solution to dryness. The yields actually obtained in this experiment were monobromo-derivative 25 per cent., dibromo-derivative 31 per cent., and tribromo-derivative 23 per cent. The total percentage is therefore only 79, but allowance has to be made for the inevitable loss due to a long process of fractional recrystallisation.

*ωωω′-Tribromo-*p*-xylene*, $CHBr_2{\cdot}C_6H_4{\cdot}CH_2Br$, separates from light petroleum (b. p. 80—90°) or from chloroform in lustrous plates melting at 106°:

0·4016 gave 0·6595 AgBr. Br = 69·88.

$C_8H_7Br_3$ requires Br = 70·0 per cent.

The compound is practically insoluble in cold ether and therefore the method used by Löw (*Annalen*, 1885, **231**, 363) for the separation of the di- and tri-bromo-derivatives by means of this solvent is not to be recommended, since both are equally insoluble in it. When boiled with an aqueous solution of potassium carbonate the tribromo-derivative is transformed into the corresponding aldehyde-alcohol. This and the other aldehyde-alcohols derived from the ortho- and meta-compounds are under investigation.

Conversion of the three ω-Bromoxylenes into the Corresponding Nitriles.

The three tolylacetonitriles were prepared from the corresponding bromo-derivatives by the action of potassium cyanide in alcoholic solution. Ninety grams of potassium cyanide were taken to every 150 grams of the bromo-compound and the alcoholic solution of the two was heated on the water-bath for four hours. The quantity of potassium cyanide is in large excess, but this was found necessary to ensure complete conversion. After the alcohol had been separated from the products by distillation on the water-bath, water was added and the nitrile extracted with ether. The residual oil after evaporating the ether was purified by distillation under the ordinary pressure and the fractions collected were 242—245° in the case of the ortho- and para-compounds and 239—242° in the case of the meta-derivative.

Ethyl β-Imino-α-cyano-γ-o-tolylbutyrate,

$C_6H_4Me\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$.

This substance was prepared by the condensation of the sodium compound of ethyl cyanoacetate and *o*-tolylacetonitrile. Twenty-three grams of sodium were dissolved in 280 grams of alcohol and the mixture, after being treated with 131 grams of *o*-tolylacetonitrile, heated on the water-bath with constant shaking for 15 hours. The reaction proceeded in the usual way, the white sodium derivative of ethyl cyanoacetate being gradually replaced by the brown, gelatinous sodium compound of the imino-nitrile. At the end of the time stated the dark-coloured product, which was almost solid, was mixed with water and the solution acidified with hydrochloric acid. The heavy oil which then separated was extracted by ether, the ethereal solution being freed from alcohol by washing with water and then further purified by thoroughly shaking with sodium carbonate solution. The ethereal solution was evaporated free from ether and distilled in a current of steam until all unchanged *o*-tolylacetonitrile had passed over, when the residue in the flask solidified on cooling. It was collected, dried on a porous plate, and recrystallised from alcohol, being obtained in colourless prisms melting at 124°:

0·1542 gave 0·3905 CO_2 and 0·0954 H_2O. C = 69·07; H = 6·83.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The yield of the ethyl salt is about 40 per cent. of the theoretical, but since the whole of the unchanged *o*-tolylacetonitrile can be recovered by steam distillation it is an easy matter to obtain more of the condensation product by repeating the above process.

*Ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate* is insoluble in alkaline carbonates and is not readily hydrolysed by boiling hydrochloric acid. The sodium carbonate washings deposited a considerable quantity of acid oil on acidifying, which was extracted with ether and isolated in the usual way. No definite products could, however, be prepared from it.

Formation of o-*Tolylacetic Acid and Malonic Acid from Ethyl β-Imino-α-cyano-γ-*o*-tolylbutyrate on Hydrolysis.*

In order to determine the constitution of this ethyl salt 5 grams were mixed with a methyl-alcoholic solution of 1½ times the calculated quantity of potassium hydroxide and the solution heated on the water-bath until a test portion was completely soluble in water. The product was then evaporated free from alcohol and the residue after dilution with water acidified with hydrochloric acid. The resulting precipitate was collected and crystallised from water, yielding colourless, silky needles melting at 88—89°:

0·1963 gave 0·5177 CO_2 and 0·1201 H_2O. C = 71·92; H = 6·79.

$C_9H_{10}O_3$ requires C = 72·0; H = 6·7 per cent.

This compound is therefore *o*-tolylacetic acid, $C_6H_4Me{\cdot}CH_2{\cdot}CO_2H$. The aqueous solution after the separation of *o*-tolylacetic acid was extracted with ether to remove the last traces of this acid and then evaporated to dryness on the water-bath. The solid residue on extraction with ether in a Soxhlet apparatus yielded a crystalline acid which, since it melted at 132° and gave acetic acid on distillation, was evidently malonic acid.

Ethyl 1-Methyl-5 : 7-naphthylenediamine-6-carboxylate, $C_{10}H_4Me(NH_2)_2{\cdot}CO_2Et$.

This substance was prepared by the action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate. Ten grams were ground to a fine powder and added gradually to five times its weight of concentrated sulphuric acid cooled to −5°. The ethyl salt dissolved at once, forming an intense brown-red solution which was poured on ice. As the strongly coloured solution mixed with the water it became first green and finally pale yellow, a reaction which is, however, best seen by diluting about 1 c.c. of the solution with one drop of water when it becomes deep olive-green. The yellow solution was rendered strongly alkaline with ammonia and then extracted with ether, giving a deep yellow, fluorescent ethereal solution which was freed from the base by shaking with dilute sulphuric acid. The acid extract on being made alkaline with ammonia gave a yellow precipitate of the base which was collected and crystallised first from alcohol and finally from light petroleum (b. p. 80—90°). It forms brilliant yellow leaflets melting at 165°:

0·1514 gave 0·3834 CO_2 and 0·0934 H_2O. C = 69·06; H = 6·82.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The solutions of ethyl 1-methyl-5:7-naphthylenediamine-6-carboxylate in all solvents exhibit strong green fluorescence. It dissolves immediately in hydrochloric acid and the solution on concentration deposits the *dihydrochloride*, $C_{14}H_{16}O_2N_2,2HCl$, in colourless needles:

0·2347 of the base required 19·6 c.c. of *N*/10 hydrochloric acid.

$C_{14}H_{16}O_2N_2$ requires 19·7 c.c.

The yield of the ethyl salt was not more than 10 per cent. of the theoretical and it was therefore necessary to ascertain the nature of the main product of the reaction, since no trace of ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate was recovered unchanged. This was ultimately found in the ammoniacal mother-liquor after the extraction of the base by ether, for when this solution was saturated with ammonium sulphate a large quantity of a yellow compound separated which proved to be the ammonium salt of a phenolic base. It was readily soluble in water and the deep yellow solution gave no precipitate on acidifying, but when it was mixed with a solution of sodium carbonate ammonia was evolved and the insoluble phenolic base separated. This substance dissolved in concentrated sulphuric acid, forming an intense reddish-brown solution which changed to green on dilution and was therefore the compound to the formation of which the colour produced in the reaction of sulphuric acid on ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate was due, since the naphthylenediamine derivative formed at the same time gives no colour with concentrated sulphuric acid. The green coloration produced when water is added to a solution of the phenolic base in concentrated sulphuric acid is due to hydrolysis, since the phenolic base is hydrolysed by boiling sodium hydroxide solution, evolving ammonia and yielding a base which dissolves in concentrated sulphuric acid, forming an intense olive-green solution. A complete investigation of these products is in progress.

1-*Methyl*-5 : 7-*naphthylenediamine*-6-*carboxylic Acid*, $C_{10}H_4Me(NH_2)_2{\cdot}CO_2H$.

The hydrolysis of ethyl 1-methyl 5:7-naphthylenediamine 6-carboxylate was effected by means of alcoholic potash. Ten grams were mixed with a solution of $1\frac{1}{2}$ times the calculated quantity of potassium hydroxide dissolved in methyl alcohol and the solution allowed to become warm on the water-bath. After some time a yellow *potassium* salt separated, the quantity of which increased on standing until the contents of the flask had become almost solid. The salt was collected, washed with a little methyl alcohol, and dried on a porous plate. It was then dissolved in water and the solution acidified with hydrochloric acid, when a colourless, crystalline precipitate separated. This was collected and recrystallised from a little warm water, from which solvent the acid separated in colourless needles which decomposed at about 137°:

0·1674 gave 0·4087 CO_2 and 0·0844 H_2O. C = 66·58; H = 5·60.
$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

1-*Methyl*-5:7-*naphthylenediamine*-6-*carboxylic acid* is readily soluble in warm water but sparingly so in cold water. The aqueous solution on boiling slowly loses carbon dioxide, the evolution being very rapid when dilute hydrochloric acid is present. It does not form salts with acids.

1-*Methyl*-5:7-*naphthylenediamine*, $C_{10}H_5Me(NH_2)_2$.

When the carboxylic acid just described is heated a few degrees above its melting point, carbon dioxide is eliminated and the above base is formed. The product is, however, always dark-coloured, and for this reason the following process was adopted. The pure carboxylic acid was dissolved in warm water, and the solution mixed with excess of hydrochloric acid and boiled on the sand-bath for fifteen minutes. At the end of this time the evolution of carbon dioxide, which was abundant at first, had ceased, and the solution was therefore made alkaline with ammonia and the precipitated base isolated by filtration. It was purified by crystallisation from water and obtained in colourless laminæ melting at 123°:

0·1738 gave 0·4877 CO_2 and 0·1082 H_2O. C = 76·53; H = 6·91.
$C_{11}H_{12}N_2$ requires C = 76·7; H = 7·0 per cent.

The crystals of the base become brown on exposure to the air.

The *dihydrochloride*, $C_{11}H_{12}N_2,2HCl$, separates from a solution of the base in concentrated hydrochloric acid in colourless, microscopic needles:

0·2295 of the base required 27·4 c.c. of $N/10$ hydrochloric acid.
$C_{11}H_{12}N_2$ requires 27·4 c.c.

The *platinichloride*, $C_{11}H_{12}N_2,H_2PtCl_6$, is formed as a yellow, crystalline precipitate on adding a solution of platinic chloride to an aqueous solution of the hydrochloride of the base:

0·2517 gave 0·1010 Pt. Pt = 40·12.

$C_{11}H_{12}N_2,H_2PtCl_6$ requires Pt = 40·4 per cent.

The *diacetyl* derivative, $C_{11}H_{10}N_2(CO{\cdot}CH_3)_2$, is best prepared by the action of acetyl chloride on the base. Two grams were boiled with a large excess of acetyl chloride in a Geissler flask until hydrogen chloride ceased to be evolved, when the solution was poured into a glass dish and evaporated in a desiccator over potash. The solid residue on crystallisation from glacial acetic acid yielded the *diacetyl* derivative in slender, colourless needles melting at 275°:

0·1815 gave 0·4672 CO_2 and 0·1029 H_2O. C = 70·21; H = 6·29.

$C_{15}H_{16}O_2N_2$ requires C = 70·3; H = 6·2 per cent.

Ethyl β-Imino-α-cyano-γ-m-tolylbutyrate, $C_6H_4Me{\cdot}CH_2{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et$.

This compound was prepared by the condensation of *m*-tolylacetonitrile with the sodium compound of ethyl cyanoacetate. One hundred and thirteen grams of ethyl cyanoacetate were added to a solution of 23 grams of sodium in absolute alcohol, and the mixture treated with 131 grams of *m*-tolylacetonitrile. No reaction took place in the cold, but on heating the white sodium compound gradually dissolved. The heating was continued on the water-bath for twelve hours, when water was added, and the solution acidified with hydrochloric acid. The heavy oil which then separated was extracted with ether, the ethereal solution washed with water and then with sodium carbonate solution, freed from ether by evaporation, and distilled in a current of steam. The whole of the unchanged nitrile passed over with the steam, leaving a residue which solidified on cooling. This solid was collected and crystallised from alcohol, yielding large, colourless, flat needles melting at 118°:

0·1573 gave 0·3980 CO_2 and 0·0953 H_2O. C = 69·01; H = 6·73.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The yield of the ethyl salt is about 40 per cent. of the theoretical, but the whole of the *m*-tolylacetonitrile unattacked can be recovered from the steam distillate. A larger yield can be obtained by continuing the time of heating to twenty-four hours, but under these conditions many by-products are formed from which the ethyl salt has to be separated by repeated recrystallisation. It is therefore advisable to heat for the shorter time, and use the recovered nitrile for a subsequent condensation. The sodium carbonate washings deposited a quantity of oil on acidifying, but no crystalline compound has as yet been isolated from it.

Formation of m-*Tolylacetic Acid and Malonic Acid by the Hydrolysis of Ethyl β-Imino-α-cyano-γ-*m*-tolylbutyrate.*

In order to effect this hydrolysis 5 grams of the ethyl salt were boiled with a methyl-alcoholic solution of one and a half times the calculated quantity of potassium hydroxide until completely soluble in water. The product was then freed from alcohol by evaporation, diluted with water, and acidified. The copious white precipitate which separated was collected and crystallised from hot water, yielding glistening needles melting at 61°:

0·2001 gave 0·5281 CO_2 and 0·1229 H_2O. C = 71·98; H = 6·82.

$C_9H_{10}O_2$ requires C = 72·0; H = 6·7 per cent.

The compound is therefore *m*-tolylacetic acid, $C_6H_4Me{\cdot}CH_2{\cdot}CO_2H$.

The aqueous filtrate was evaporated to dryness, and the residue extracted with ether in a Soxhlet apparatus. The ethereal solution, after drying and evaporating, gave a crystalline acid which melted at 132° and yielded acetic acid on distillation. It was therefore malonic acid.

Ethyl 2-*Methyl*-5 : 7-*naphthylenediamine*-6-*carboxylate*, $C_{10}H_4Me(NH_2)_2{\cdot}CO_2Et$.

This compound was prepared by the action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate. Ten grams of the finely-powdered ethyl salt were slowly added to 50 grams of concentrated sulphuric acid cooled in a mixture of ice and salt to −5°. The ethyl salt rapidly dissolved and the strong acid became pale red, but it was evident that the colour-producing constituent was present only in small amount. When all the ethyl salt had been added, the solution was allowed to stand for three to four minutes and then poured on ice. The colourless solution thus obtained was then rendered alkaline by means of ammonia, and the deep yellow precipitate which then formed extracted by ether. The yellow ethereal solution, which exhibited marked green fluorescence, on being shaken with dilute sulphuric acid became colourless, and the sulphuric acid extract on being made alkaline yielded a yellow, crystalline precipitate of the base. *Ethyl* 2-*methyl*-5 : 7-*naphthylenediamine*-6-*carboxylate* is best purified by recrystallisation, first from ethyl alcohol, and then from ether, when it is obtained in clusters of yellow needles melting at 105°. It may also be recrystallised from light petroleum (b. p. 80—90°).

0·1573 gave 0·3968 CO_2 and 0·0952 H_2O. C = 68·80; H = 6·72.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The yield of this compound is about 80—85 per cent. of the theoretical.

The *dihydrochloride*, $C_{14}H_{16}O_2N_2,2HCl$, is obtained in almost colourless needles on dissolving the ethyl salt in concentrated hydrochloric acid, and allowing the solution to stand:

0·2135 of the base required 18·1 c.c. of *N*/10 hydrochloric acid.
$C_{14}H_{16}O_2N_2$ requires 18·0 c.c.

When ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate is dissolved in concentrated sulphuric acid at the ordinary temperature the solution becomes cherry-red, and when the strong acid is poured on ice the solution, instead of being colourless, is pale yellow. When worked up in the manner described above the yield of the naphthalene derivative is found to be only about 65 per cent. of the theoretical, and on adding ammonium sulphate to the solution after extraction with ether a considerable quantity of a yellow ammonium salt is precipitated. This ammonium salt gives a cherry-red solution in concentrated sulphuric acid, which changes to yellow on dilution without the formation of intermediate colorations, and on boiling with aqueous sodium carbonate is converted with loss of ammonia into a base insoluble in water, This compound is therefore a phenolic base similar to that formed to so large an extent by the action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate.

In one experiment it was not found possible to prevent the formation of a deep red colour on dissolving the ethyl salt in sulphuric acid at $-5°$. It was ultimately found, however, that the formation of the colour was due to the presence of traces of the ortho-derivative mixed with the meta-compound. It was evident therefore that some *o*-xylene must have been present in the *m*-xylene used. The small quantity of the ortho-derivative was, however, readily eliminated by recrystallisation when the pure meta-compound behaved in the manner described above.

Oxidation of Ethyl 2-*Methyl*-5 : 7-*naphthylenediamine*-6-*carboxylate to* 4-*Methylphthalic Acid.*—This oxidation was carried out in order to establish the constitution of ethyl 2-methyl-5 : 7-naphthylenediamine-6-carboxylate, since, as was pointed out in the introduction, the formation of the naphthalene ring from ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate could also take place in the ortho-position with respect to the methyl group, in which case ethyl 1-methyl-6 : 8-naphthylenediamine-7-carboxylate would be formed, which on oxidation would give 3-methylphthalic acid. Ten grams of the ethyl salt were dissolved in excess of dilute sulphuric acid and the solution heated to boiling. Twenty-five grams of potassium dichromate were then dissolved in water, and the two hot solutions mixed, the whole being finally heated to boiling for a short time on the sand-bath. The black-brown precipitate was then filtered and dried on a porous plate, after which it was extracted thoroughly with ether. The substance insoluble in ether was then boiled with sodium carbonate solution and filtered, when the filtrate, on acidifying, deposited a solid acid which, when crystallised from water, formed colourless prisms melting at 152°.

0·2219 gave 0·4872 CO_2 and 0·0901 H_2O. C = 59·88; H = 4·51.

$C_9H_8O_4$ requires C = 60·0; H = 4·4 per cent.

The acid is therefore 4-methylphthalic acid (compare Niementowski, *Monatsh.*, 1891, **12**, 624, and Young, *Ber.*, 1892, **25**, 2108). It was further identified by converting it into the anhydride (melting at 92°) by means of acetyl chloride.

The ethereal solution from the black chromic acid precipitate gave, on evaporation, a dark-coloured resin, from which no definite compound could be isolated.

2-*Methyl*-5 : 7-*naphthylenediamine*-6-*carboxylic Acid*, $C_{10}H_4Me(NH)_2 \cdot CO_2H$.

Ethyl 2-methyl-5 : 7-naphthylenediamine-6-carboxylate is not so readily hydrolysed by methyl-alcoholic potash as are its isomerides, and must be heated for a longer time before the reaction is complete. Five grams were added to a solution containing $1\frac{1}{2}$ times the calculated quantity of potassium hydroxide in methyl alcohol, and heated on the water-bath for two hours. On cooling and standing, a crystalline *potassium* salt separated which was collected, washed quickly with a little methyl alcohol, in which, however, the salt is very soluble, dried, and dissolved in water. The pale yellow, aqueous solution gave a precipitate of the *acid* on acidifying, which was collected and crystallised from warm water. It forms colourless, microscopic needles which decompose at about 130°:

0·1753 gave 0·4288 CO_2 and 0·0893 H_2O. C = 66·71; H = 5·66.

$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

The acid does not form salts with mineral acids.

2-*Methyl*-5 : 7-*naphthylenediamine*, $C_{10}H_5Me(NH_2)_2$.

The carboxylic acid readily loses carbon dioxide even on boiling with water. It was transformed into the above base by boiling an aqueous solution, which had been mixed with hydrochloric acid, for fifteen minutes, cooling, filtering and making the filtrate alkaline with ammonia. The crystalline precipitate of the base which then separated was recrystallised from water and obtained in glistening plates melting at 137°:

0·1822 gave 0·5119 CO_2 and 0·1144 H_2O. C = 76·63; H = 6·97.

$C_{11}H_{12}N_2$ requires C = 76 7; H = 7·0 per cent.

The *dihydrochloride*, $C_{11}H_{12}N_2,2HCl$, separates from a solution of the base in concentrated hydrochloric acid in colourless prisms:

0·2107 of the base required 25·1 c.c. of $N/10$ hydrochloric acid.

$C_{11}H_{12}N_2$ requires 25·2 c.c.

The *platinichloride*, $C_{11}H_{12}N_2,H_2PtCl_6$, is formed as a yellow, crystalline precipitate on adding a solution of platinic chloride to an aqueous solution of the hydrochloride of the base:

0·2619 gave 0·1055 Pt. Pt = 40·20.

$C_{11}H_{12}N_2,H_2PtCl_6$ requires 40·4 per cent.

The *diacetyl* derivative, $C_{11}H_{10}N_2(CO\cdot CH_3)_2$, is best prepared by the action of acetyl chloride on the base. One gram was boiled in a Geissler flask with excess of acetyl chloride until the evolution of hydrogen chloride had ceased, when the excess of chloride was evaporated and the solid residue crystallised from glacial acetic acid. It forms slender needles melting at 256°:

0·1942 gave 0·4991 CO_2 and 0·1101 H_2O. C = 70·09; H = 6·29.

$C_{15}H_{16}O_2N_2$ requires C = 70·3; H = 6·2 per cent.

*Ethyl β-Imino-α-cyano-γ-*p*-tolylbutyrate*, $C_6H_4Me\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$.

This ethyl salt was prepared by the condensation of *p*-tolylacetonitrile with the sodium compound of ethyl cyanoacetate. Twenty-three grams of sodium were dissolved in 280 grams of alcohol and the solution mixed with 113 grams of ethyl cyanoacetate. One hundred and thirty-one grams of *p*-tolylacetonitrile were then added and the whole heated on a water-bath for twelve hours. The reaction proceeded in the normal manner and at the end of the time of heating the flask was filled with the gelatinous sodium compound of the condensation product. Dilute hydrochloric acid was added and the oil extracted with ether, the ethereal extract being washed with water and then with sodium carbonate solution. The ether was then evaporated and the residue distilled in a current of steam until the whole of the unchanged *p*-tolylacetonitrile had passed over, when the residue remaining in the flask completely solidified on cooling. The solid was collected and crystallised from alcohol, being obtained in exceptionally large, transparent, rhombic plates melting at 117°:

0·1652 gave 0·4157 CO_2 and 0·0996 H_2O. C = 68·63; H = 6·69.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The yield of the para- is greater than that of either the ortho- or meta-compound, being 60—65 per cent. of the theoretical. The sodium carbonate washings from the ethereal solution deposited an oil on acidifying. It was collected, but as yet no definite product has been isolated from it.

Formation of p-*Tolylacetic Acid and Malonic Acid from Ethyl β-Imino-α-cyano-γ-*p-*tolylbutyrate on Hydrolysis.*

The constitution of ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate was determined in the usual manner by alkaline hydrolysis. Five grams were boiled with a methyl-alcoholic solution of one and a half times the calculated quantity of potash until completely soluble in water, when the alcohol was evaporated and the aqueous solution of the residue acidified with hydrochloric acid. The resulting white precipitate was collected and crystallised from water, yielding colourless needles melting at 91°:

0·1982 gave 0·5227 CO_2 and 0·1218 H_2O. C = 71·92; H = 6·82.

$C_9H_{10}O_2$ requires C = 72·0; H = 6·7 per cent.

The acid is therefore *p*-tolylacetic acid, $C_6H_4Me\cdot CH_2\cdot CO_2H$.

The aqueous solution after the extraction of the above acid was evaporated to dryness on the water-bath and the solid residue extracted with ether in a Soxhlet apparatus. The ethereal extract on drying and evaporating yielded a solid acid which melted at 132° and gave acetic acid on distillation. It was therefore malonic acid.

Ethyl 2-Methyl-6:8-naphthylenediamine-7-carboxylate, $C_{10}H_4Me(NH_2)_2\cdot CO_2Et$.

The action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate is very characteristic. When a trace of the ethyl salt is added to about 1 c.c. of concentrated sulphuric acid an intense magenta-red solution is produced, which on the addition of a drop of water changes to violet, another drop changes it to blue, a further drop to green, and finally, on more water being added, the solution becomes yellow. It is impossible to prevent the formation of this colour even when the reaction is carried out at −10°.

The above naphthalene derivative was prepared in the following way: Ten grams were ground to a fine powder and gradually added to 50 grams of concentrated sulphuric acid cooled to −10° in a mixture of ice and salt. The ethyl salt readily dissolved, forming an intense magenta solution which was poured on ice, when the colour was discharged, a yellow solution being ultimately formed. Ammonia was added until the solution was alkaline and the resulting precipitate was extracted with ether. The ethereal solution was then washed with water and the ethyl salt extracted from it by shaking with dilute sulphuric acid. The acid extract on being made alkaline with ammonia deposited the free ethyl salt, which was purified by crystallisation first from ethyl alcohol and finally from light petroleum (b. p. 80—90°), being obtained in clusters of bright yellow needles melting at 101°:

0·1573 gave 0·3976 CO_2 and 0·0951 H_2O. C = 68·94; H = 6·71.

$C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·6 per cent.

The *dihydrochloride*, $C_{14}H_{16}O_2N_2,2HCl$, can be obtained in almost colourless plates on dissolving the ethyl salt in concentrated hydrochloric acid and allowing the solution to stand:

0·2011 of the base required 16·9 c.c. of *N*/10 hydrochloric acid.

$C_{14}H_{16}O_2N_2$ requires 16·9 c.c.

The yield of the ethyl salt is scarcely 9 per cent. of the theory, and consequently comparatively large quantities of material had to be employed in order to obtain sufficient for the research. The chief product of the reaction can be isolated as a soluble ammonium salt on saturating the ammoniacal mother-liquor, after the extraction of the ethyl salt, with ammonium sulphate. This substance is the ammonium salt of a phenolic base, and when dissolved in concentrated sulphuric acid gives the colour reaction exhibited by ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate with this reagent. It is therefore to the formation of this substance that the colour reaction of the ethyl salt is due. The ammonium salt yields the free phenolic base on treatment with sodium carbonate solution, and the free base on boiling with sodium hydroxide is hydrolysed, evolving ammonia and yielding another base, which dissolves in concentrated sulphuric acid, producing an intense blue coloration. The change from magenta-red to blue on adding a drop of water to a solution of ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate in concentrated sulphuric acid is probably due therefore to the hydrolysis of the phenolic base first formed in the reaction. A complete examination of these compounds is in progress.

2-*Methyl*-6 : 8-*naphthylenediamine*-7-*carboxylic Acid*,
$C_{10}H_4Me(NH_2)_2\cdot CO_2H$.

Ethyl 2-methyl-6 : 8-naphthylenediamine-7-carboxylate is readily hydrolysed when warmed with a methyl-alcoholic solution of one and a half times the calculated quantity of potassium hydroxide, and the product on cooling deposits the sparingly soluble *potassium* salt of the acid. It was collected, washed quickly with a little methyl alcohol, dried, and dissolved in water. On acidifying this solution the free *acid* was precipitated and was purified by crystallisation from warm water. It forms clusters of colourless needles decomposing at about 147°:

0·1601 gave 0·3901 CO_2 and 0·0832 H_2O. C = 66·45; H = 5·69.

$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

The acid does not form salts with mineral acids.

2-*Methyl*-6 : 8-*naphthylenediamine*, $C_{10}H_5Me(NH_2)_2$.

The carboxylic acid readily loses carbon dioxide when boiled with water and passes into the above base, the transformation being best effected by boiling a solution of the acid in dilute hydrochloric acid for fifteen minutes on the sand-bath. The solution thus obtained, on being rendered alkaline with ammonia, gives a precipitate of the base which can be purified by crystallisation from water, yielding small plates melting at 119°:

0·1787 gave 0·5021 CO_2 and 0·1111 H_2O. C = 76·63 ; H = 6·90.

$C_{11}H_{12}N_2$ requires C = 76·7 ; H = 7·0 per cent.

The *dihydrochloride*, $C_{11}H_{12}N_2,2HCl$, separates as a microcrystalline precipitate on allowing a solution of the base in concentrated hydrochloric acid to stand:

0·2311 of the base required 27·5 c.c. *N*/10 hydrochloric acid.

$C_{11}H_{12}N_2$ requires 27·6 c.c.

The *platinichloride*, $C_{11}H_{12}N_2,H_2PtCl_6$, is precipitated in yellow crystals on adding a solution of platinic chloride to an aqueous solution of the hydrochloride of the base:

0·2738 gave 0·1103 Pt. Pt = 40·28.

$C_{11}H_{12}N_2,H_2PtCl_6$ requires Pt = 40·4 per cent.

The *diacetyl* derivative, $C_{11}H_{10}N_2(CO{\cdot}CH_3)_2$, is formed when the base is boiled with an excess of acetyl chloride until the evolution of hydrogen chloride has ceased. The excess of acetyl chloride is removed by evaporation, and the residue is purified by crystallisation from glacial acetic acid, from which solvent it separates in colourless prisms melting at 263°:

0·1808 gave 0·4641 CO_2 and 0·1027 H_2O. C = 70·02 ; H = 6·31.

$C_{15}H_{16}O_2N_2$ requires C = 70·3 ; H = 6·2 per cent.

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MANCHESTER UNIVERSITY.

CLXI.—*The Atomic Volumes of Phosphorus.*

By Edmund Brydges Rudhall Prideaux, M.A., D.Sc.

The relation between the atomic and molecular volumes of liquid elements and compounds has been the subject of much inquiry, most of which has been concerned with the assignment of an average value to the atomic volumes as shown in carbon compounds, starting from atomic volumes of carbon and hydrogen deduced from the difference of molecular volume brought about by the addition of CH_2 to the molecule.

The universality of an approximately additive relation and the frequent inexactness of this approximation point, the former to some far-reaching regularity, and the latter to occasional disturbing influences. The nature of these is known, and most of them can be got rid of by a choice of the compounds to be investigated.

Firstly, by dealing only with compounds containing few atoms not only is the influence of isomerism eliminated, but also that increased inaccuracy due to the summation of several atomic volumes, each affected with an error.

Then if the field is further restricted to compounds containing only two elements, one at least of which is univalent, a further source of doubt is removed; that due to the variable atomic volumes of, for example, oxygen in the combinations $R{\cdot}O{\cdot}R$ and $R{:}O$.

The present, then, is the first instalment of a comparison between the atomic volumes of R and X in the free state with those of R and X in compounds RX_m and RX_n.

Although the effect of valency in modifying the atomic volume of phosphorus cannot at present be studied with the closeness which experimental accuracy would allow, yet every effort has been made to reduce errors of measurement to a minimum in order that the results should be available for a quantitative discussion at a future date.

The investigation consists of a statement of the best available values for the atomic volumes of chlorine, phosphorus, phosphorus trichloride, and phosphorus pentachloride at their respective boiling points, and a comparison of the values deduced for combined phosphorus.

Chlorine.—The density of liquid chlorine at −33·6° is 1·557 (Knietsch, *Annalen*, 1890, **259**, 100). This value is probably correct to 0·001 of a unit, and the atomic volume is therefore 22·76 ± 0·01.

Phosphorus.—The specific volumes of liquid phosphorus have been determined from 26° to 50°. At higher temperatures there is the single value 20·9 ± 0·4 for the atomic volume of phosphorus at its boiling point (Ramsay and Masson, Trans., 1881, **39**, 50). The value found below is in substantial agreement with this. It was arrived at by a dilatometric method, and the necessary calculations have also furnished an equation for the coefficient of expansion of liquid phosphorus at temperatures above 60°.

EXPERIMENTAL.

The expansions of phosphorus and phosphorus pentachloride are necessarily measured in sealed tubes. The dilatometers employed were etched with scales of millimetres and calibrated with mercury. The bulbs held from 0·3 to 0·5 c.c. and 1 cm. length of the tubes about 0·006 c.c. The position of the meniscus could easily be read within 0·5 mm. = 0·0003 c.c. The volumes are thus correct to one part in 1000. After exactly the right quantity had been placed in the tube, it was in all cases evacuated and sealed off.

In subsequent operations, therefore, the substance was confined under the pressure of its own vapour.

The vapour pressures attained, up to and even somewhat beyond the boiling point, are not of such an order as to have any appreciable effect on the volume of the liquid.

The method was tested in practice by a determination of the specific gravity of liquid sulphur at various temperatures. The results were in satisfactory agreement with previous work. A similar agreement will be found in that part of the present experiments on phosphorus which covers the same ground as previous work.

The temperatures were read on a thermometer which had been standardised: (1) By comparison with a standard thermometer at 18°; (2) in steam, and (3) in the vapour of boiling bromoform.

Up to 95° a water-bath was used, at higher temperatures a cylindrical air-bath of the Lothar Meyer type. A comparison was made on several occasions between the temperatures as read in this bath with those at which the liquid attained the same volume in a bath of well-stirred sulphuric acid. The agreement was satisfactory.

The purified phosphorus employed was dried by melting it in a vacuum, dry carbon dioxide was admitted into the containing tube, and the calibrated dilatometer introduced with its open end in contact with the phosphorus and filled by successive evacuations followed by admissions of dry carbon dioxide.

Volumes and temperatures of liquid phosphorus were read through a telescope. The tube was then weighed and broken, precautions being taken to lose no glass dust. The pieces were freed from phosphorus by repeated boiling with water, dried, and weighed. The difference gave the weight of phosphorus as 0·7669 gram. The degree of accuracy with which such a tube could be weighed before and after breaking was tested by a blank experiment and found to be within 2 milligrams. The weight of phosphorus is therefore correct within 1 part in 380.

These volumes of liquid phosphorus at 15 temperatures were then calculated from the scale readings, allowing in each separate case for the different expansions of the glass. They were first plotted against temperatures on squared paper. A short extrapolation gave the volume at 44° as 0·4384 c.c.; the specific gravity is therefore 1·749. The specific gravity of liquid phosphorus at 44·2° compared with that of water at 4° is given as 1·7555 (Damien, 1881).

From these volumes and temperatures an expansion formula was then calculated by the method of least squares. Coefficient of expansion between 50° and 235°:

$$V_t = V(1 + 0{\cdot}000505t + 0{\cdot}0_6118t^2).$$

The actual volume of phosphorus at 50° was 0·4396. By the above formula this becomes 0·4957 at 290°, the specific volume therefore being 0·6464 and the atomic volume 20·04.

A consideration of the sources of error affecting this determination shows that the greatest is that in the atomic weight.

The atomic volume of phosphorus at its boiling point is therefore correct within 0·1 of a unit.

Phosphorus Pentachloride.—Although this compound sublimes without melting when heated in the air, yet a very slight increase of pressure suffices to liquefy it. The comparison temperature being that at which the vapour pressure becomes equal to 1 atmosphere, the volume which liquid pentachloride would occupy at this temperature has to be obtained by a short extrapolation of the curve which represents the contraction of the liquid in cooling from a temperature some 25° higher.

So close does the temperature of liquefaction under its own vapour pressure lie to the subliming point of phosphorus pentachloride that one may substitute for the extrapolated volume the actual volume of the liquid just before solidification without making a difference of more than 0·6 of a unit in the molecular volume.

The subliming point of phosphorus pentachloride is given as 160°; a thermometer immersed in the vapour of phosphorus pentachloride subliming freely and condensing on the bulb remains steady at this temperature, which is probably the comparison temperature sought, and is certainly the lower limit of this temperature, the upper limit being furnished by the following observation. When liquid phosphorus pentachloride is slowly cooled it begins to solidify at 162°, as is seen by the rapid decrease in volume and the appearance of minute crystals. Since the compound is incapable of existing as a liquid under atmospheric pressure the vapour pressure of phosphorus pentachloride must exceed atmospheric at temperatures above 162°.

The phosphorus pentachloride used for these experiments was redistilled once in a current of dry chlorine and then again in dry carbon dioxide containing a little chlorine. The product was analysed, both chlorine and phosphorus being estimated, the latter as $Mg_2P_2O_7$:

Found, $P = 14·7$; $Cl = 85·3$.
PCl_5 requires $P = 14·87$; $Cl = 85·13$ per cent.

The dilatometers, made of the same capillary tubing as that used for phosphorus, were calibrated and broken in the manner already described. The properties of phosphorus pentachloride introduced special difficulties in the filling process, and three experiments were carried out before a quantity of phosphorus pentachloride was introduced exactly sufficient to give a direct reading of the volume at 160°. The extrapolated results of these gave values of the specific gravity at 160—165° ranging from 1·58 to 1·62.

The correct value at 160° is 1·601 from the fourth experiment.

The volumes were read through a telescope both with rising and falling temperatures. The readings did not differ by more than 0·15 of a scale division = 0·00066 c.c.

The dilatometer was then weighed and broken and the phosphorus pentachloride dissolved under water in a stoppered tube. The hydrochloric acid was estimated in this water, and hence the weight of pentachloride. The washed pieces of tube were dried and weighed and the weight of phosphorus pentachloride thus also obtained by difference:

PCl_5 calculated from $AgCl = 0·4739$.
PCl_5 by weighing before and after $= 0·4736$.

The dilatometer scale readings plotted against temperatures gave nearly a straight line, the curvature being so slight that the coefficient of expansion from 160° to 190° may be taken as approximately linear.

The true volumes were then calculated for seven temperatures, allowing in each case for the expansion of glass and for the variation in the bore of the tube:

Temperature.	Volume in c.c.	Temperature.	Volume in c.c.
160°	0·2932	180°	0·2995
165	0·2948	185	0·3014
170	0·2964	190	0·3034
175	0·2979		

From these values the coefficient of expansion was calculated by the method of least squares.

From 160° to 190° phosphorus pentachloride expands according to the equation:

$$V_{160^\circ+t} = 1 + 0{\cdot}00107t.$$

The volume at 160° is found from this equation to be 0·2932 c.c. and the specific volume of phosphorus pentachloride = 0·2932/0·4737 = 0·629.

On consideration of the possible errors it was seen that the molecular volume deduced from this was correct within 0·4 of a unit:

$$\begin{array}{rl} PCl_5 = & 128{\cdot}9 \\ 5Cl = & 113{\cdot}8 \\ \hline P^{V} = & 15{\cdot}1 \pm 0{\cdot}5. \end{array}$$

So that the atomic volume of quinquevalent phosphorus is some 5 units less than that of elementary phosphorus.

From the molecular volume 93·34 of phosphorus trichloride (Thorpe, Trans., 1880, **37**, 378) is subtracted 3 × 22·76, and the remaining atomic volume of P^{III} is estimated to be correct within 0·4 of a unit.

We have therefore the following relations between P (element), P^{III} (in PCl_3), and P^{V} (in PCl_5).

$$\begin{array}{rrll} & \text{Atomic volume.} & & \\ P^{III} = & 25{\cdot}06 & \text{within} & 0{\cdot}4 \\ P^{V} = & 15{\cdot}10 & ,, & 0{\cdot}5 \\ \cline{2-2} & 2/40{\cdot}16 & & \\ \cline{2-2} \text{Mean of } P^{III} \text{ and } P^{V} = & 20{\cdot}08 & \text{within} & 0{\cdot}5 \\ \text{Elementary phosphorus} = & 20{\cdot}04 & ,, & 0{\cdot}1 \end{array}$$

So that within the limits of experimental error the atomic volume of liquid phosphorus at its boiling point is the exact mean between those of ter- and quinque-valent phosphorus in the chlorides at their boiling points.

HERIOT-WATT COLLEGE,
EDINBURGH.

CLXII.—*Indican. Part I.*

By ARTHUR GEORGE PERKIN and WILLIAM POPPLEWELL BLOXAM.

ACCORDING to the early researches of Chevreul (*Ann. Chim.*, 1808, **66**, 8, and 1808, **68**, 284), and of Giradin and Preisser (*Journ. Pharm.*, 1840, **26**, 344), the colouring principle of indigotin present in indigo-yielding plants was considered to consist of indigo-white, and this theory remained uncontradicted until Schunck (*Phil. Mag.*, 1855, [iv], **10**, 74, and *ibid.*, 1858, **15**, 127) isolated from the *Isatis tinctoria* and *Polygonum tinctorium* a glucoside which he named indican. This compound, $C_{26}H_{31}O_{17}N$, on hydrolysis, gave indigotin and a sugar, indiglucin,

$$2C_{26}H_{31}O_{17}N + 4H_2O = C_{16}H_{10}O_2N_2 + 6C_6H_{10}O_6,$$

and it appeared that during the reaction the indigotin at first formed was reduced to indigo-white, and subsequently reoxidation took place. Later, however, Schunck and Römer (*Ber.*, 1879, **12**, 2311) showed that indican, when hydrolysed in the absence of air, gave a product which, when treated with oxidising agents, did not yield indigotin.

Much more recently, Marchlewski and Radcliffe (*J. Soc. Chem. Ind.*, 1898, **17**, 434) suggested that indican had possibly the formula $C_{14}H_{17}O_6N$, and that, on hydrolysis, glucose and indoxyl were formed, the latter on oxidation being naturally converted into indigotin,

$$C_{14}H_{17}O_6N + H_2O = C_8H_7ON + C_6H_{12}O_6.$$

As a result of the communication of Marchlewski and Radcliffe, Hazewinkel, the Director of the experimental station for indigo, Klaten, Java (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512), gave an account of a research concluded in 1898, which he had hitherto considered to be to the interest of the Java planters to keep secret. In this important paper he gives proof that indican is an indoxyl glucoside, and that the sugar obtained from it is dextrose. The elaborate researches of Beyerinck, van Romburgh, and other Dutch chemists indicated that indican was far more stable than Schunck supposed, and eventually led to the isolation of this glucoside in a crystalline condition from the *Indigofera leptostachya* and *Polygonum tinctorium*, by Hoogewerff and ter Meulen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 520). Analyses and a molecular weight determination of their substance showed that it possessed the formula $C_{14}H_{17}O_6N$, and when crystallised from water contained $3H_2O$. By passing air through a hot solution of the indican in dilute hydrochloric acid they obtained 91 per cent. of the theoretical yield of indigotin, which appeared, however, to contain some indirubin, and of the purity of the mixture they could not be certain. The identity of the sugar formed during the reaction they proposed to ascertain when they possessed sufficient glucoside for the purpose.

In a paper by Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 101) "On the Formation of Indigo from Woad," this chemist discusses Schunck's well-known paper on the same subject (*loc. cit.*), and points out that the indigo-yielding substance contained in this plant is not, as Schunck regarded it, identical with the indican present in the *Polygonum tinctorium*. This colouring principle of woad Beyerinck names isatan, and shows that this compound, unlike indican, is decomposed in feebly alkaline solutions, whereas indican itself is stable in concentrated alkaline liquids. In the presence of acids both isatan and indican are hydrolysed, but indican with greater difficulty, a point which is specially evident when acid salts are employed. Isatase, the specific enzyme of woad, does not act on indican, and isatan, on the other hand, is unaffected both by the indigo enzyme or by common bacteria. Schunck (*Chem. News*, 1900, **82**, 176) considered that the crystalline indican of Hoogewerff and ter Meulen was not the substance obtained by him, and should not be considered as a pure variety of it, but was rather derived from it by extracting the plant with a hot solvent and the use of chemicals. He preferred to name his compound *a*-indican and theirs *b*-indican. With regard to Beyerinck's criticisms, he was at a loss to understand the views of this author.

Finally, Bergtheil (Trans., 1904, **85**, 877) did not find it possible to prepare crystalline indican in the manner described by Hoogewerff and ter Meulen.

In connexion with the study of natural indigo and its formation from the plant, which has been in progress in this laboratory for the past two years, it was necessary to obtain some quantity of pure indican for the elucidation of several points in this work. Without the possession of this substance, any exact knowledge of the efficiency of the Indian process could not be determined, for the methods of leaf analysis there employed have hitherto been based upon no standard.

The specimens of leaf investigated were collected and forwarded to us from India by Government botanists, and although it is only likely that the samples had deteriorated to some extent during the collection and drying operations, they contained considerable quantities of indican.

We are greatly indebted to Prof. Beyerinck, of Delft, and Prof. van Romburgh, of Utrecht, for specimens of crystalline indican, and we also express our thanks to Messrs. Burroughs Wellcome and Co. for very kindly undertaking the extraction of a considerable quantity of the air-dried leaves of the *Indigofera Sumatrana*, and to Dr. G. Barger for his interest in the matter.

EXPERIMENTAL.

For the preparation of indican, Hoogewerff and ter Meulen (*loc. cit.*) employed the *Indigofera leptostachya* and *Polygonum tinctorium*, and obtained 5 grams of the pure glucoside from 17 kilograms of the plant. The essentials of their process are as follows:—The plant is extracted with hot water, certain impurities precipitated with baryta water, and the solution evaporated to dryness. A concentrated methyl-alcoholic extract of the residue is treated with ether to precipitate non-nitrogenous compounds, the purified liquid evaporated, and the product dissolved in a little water. The filtered and concentrated solution on standing deposits crystals of indican.

During a careful study of this ingenious method, both with the *Indigofera Sumatrana* and *I. arrecta*, small quantities of crystalline indican were isolated, but it was soon evident that the operations, although of a simple character, became most tedious when working with large quantities of leaf extract, and, moreover, that in our hands a considerable loss of colouring principle took place towards the end of the evaporation process. The method was accordingly abandoned, because the labour involved in preparing any large quantity of the glucoside in this manner would be very great, and because it appeared likely that by studying the solvent properties of the crystalline indican we possessed, a simpler process could be devised. Experiment indicated that acetone would be suitable for the removal of the colouring principle from the leaf, and especially so as it was observed that the viscous by-products which had been isolated from the plant in the earlier work were but slightly attacked by this solvent. As a result, this selection was justified, and the following simple method originated.

One thousand grams of the leaves and stems of the *Indigofera Sumatrana* (analysed previously and estimated to yield 3·13 per cent. of indigotin) were treated in a large bottle with 4 litres of acetone, the mixture being occasionally shaken during seven days. Up to the present, this operation has always been carried out in the cold, for although this is probably not an essential feature for success, it proceeds so satisfactorily that it has been adopted throughout.

The green-coloured acetone solution was then filtered, the residual leaf rinsed with the solvent, and the liquid evaporated in the first operations by means of a vacuum at the ordinary temperature to a volume of about 150 c.c. In subsequent experiments, however, the acetone was removed by distillation on the steam-bath in the usual manner. To this residue about ten times its volume of light petroleum was added, causing the deposition of a yellowish-brown, viscous precipitate, which was repeatedly agitated with small quantities of light petroleum until a green-coloured extract was no longer formed. The product, on treatment with water, yielded, in the earlier experiments, a pale yellow liquid containing some quantity of grey matter in suspension, which could readily be removed by filtration, but with the more recent samples of plant the precipitate at this stage was too viscous to permit of separating the solid matter in this way. In such cases, decantation was resorted to, and the solution was clarified by agitation with ether, as but little indican is dissolved by this solvent. The clear aqueous liquid (A), after removal of dissolved ether under reduced pressure, was decanted from a small quantity of tarry deposit, treated with 10 c.c.* of $N/2$ sodium carbonate, to neutralise plant acids, and placed in a vacuum desiccator over sodium hydroxide. Within a few hours the sides of the containing vessel became coated with crystals, and in about three days a semi-solid, crystalline mass was obtained. The product was collected on a Buchner funnel and drained on porous tile; when dry, it weighed 16·40 grams. The mother liquor, again evaporated in a similar manner, gave a further 6·415 grams of the glucoside.

The residual liquid was still rich in indican, but on concentration was too viscid for filtration, and it is here that a somewhat serious loss of substance occurs. To obviate this as far as possible, the mixture, dissolved in water, was treated with finely-powdered potassium sulphate, which caused the precipitation of a brown, tarry impurity, together with some quantity of the glucoside. The solution was evaporated to dryness in a vacuum, the residue extracted with acetone, the solvent removed from the extract, and the crude indican crystallised from water. In this way, approximately 2 grams of the substance were recovered.

The residual leaf was again submitted to two extractions with acetone, by which means respectively 3·654 and 3·17 grams of indican were obtained. Accordingly, 1000 grams of leaf yielded 31·66 grams of this substance, and this quantity could have been enhanced by a further digestion of the leaf material, preferably with boiling acetone. Analysis showed, for instance, that it still contained 1·8 per cent. of glucoside, but as the object of the work was the rapid preparation of a large quantity of indican, this residue was not again extracted.

As a rule, only one digestion of the leaf with acetone was carried out, and the highest yield as yet obtained in this single operation was 32·5 grams of the substance from 1250 grams of raw material. By the adoption of a continuous method of working, a weekly return of about 30 grams of the glucoside was obtained, even during the summer, which would no doubt have been materially increased if the operations had been conducted in the winter season.

The main sources of the defective yield are, no doubt, to be accounted for in the final mother liquors, and by the draining of the crude substance on tile, and this is impossible to avoid with so soluble a compound as indican; on the other hand, some loss undoubtedly does occur during the prolonged evaporation of the aqueous liquid in a vacuum, for this, which at first possesses a pale yellowish-brown tint, soon becomes darker, and if left for several days the discoloration rapidly increases.

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* The amount of alkali necessary varies with the sample of plant employed. It is very important that sufficient be added to prevent formation of indigotin, but excess, on the other hand, causes gelatinisation.

The indican, when dry, consisted of an almost colourless mass of silky needles and was usually free from indigotin, but sometimes possessed a faint pink colour. For purification it was dissolved in warm water (1 gram in 4 c.c.), the solution allowed to cool in melting ice, and the crystals which separated, collected by the aid of the pump. A second crystallisation (1 gram in 5 c.c. of water) yielded, as a rule, the pure compound, which, when dry, melted at 57—58°.

The melting point given by Hoogewerff and ter Meulen for their product in this condition is 51°, and caused at first the supposition that the indoxyl glucoside present in the *I. Sumatrana* was distinct from that occurring in the plants they examined. An examination, however, of the preparations given to us by Profs. Beyerinck and van Romburgh showed that after crystallisation from water the melting point was 57—58° in each case, and it is therefore to be presumed that the figure 51° is the result of a clerical error.

Hoogewerff and ter Meulen further state that when indican, crystallised from water, is dried over sulphuric acid in a vacuum, it melts at 100—101°, and is then in the anhydrous condition. Experiment has shown, however, that although 100—101° is approximately the melting point of indican which has been dried in this manner, this is not the melting point of the anhydrous substance. For instance, when indican melting at 57—58° is heated above this point, it gradually resolidifies, and the crystalline mass thus obtained melts at 176—178°. This reaction is best observed by exposing the indican melting at 57—58° to the heat of the water-oven in a flat dish, a hard, crystalline cake being formed after some hours, and this solidification occurs much more rapidly at 110°. No decomposition, as stated by Hoogewerff and ter Meulen, beyond a slight discoloration, was observed by heating the glucoside thus treated above 100°, until near or about its melting point, but these, however, are the only details in which our work is at variance with that of these chemists.

To determine the water of crystallisation, the indican was heated for some hours in the steam-oven, then at 110°, until constant, and finally at 160°:

Found, $H_2O = 15{\cdot}25$, $15{\cdot}16$, $15{\cdot}07$, $15{\cdot}42$.

$C_{14}H_{17}O_6N,3H_2O$ requires $H_2O = 15{\cdot}47$ per cent.

Analyses of the anhydrous indican gave:

C = 56·81; 56·72; H = 6·05; 5·94; N = 4·83.

$C_{14}H_{17}O_6N$ requires C = 56·94; H = 5·76; N = 4·75 per cent.

In an experiment during which air-dried indican previously crystallised from water was exposed in a vacuum over sulphuric acid until constant, it lost 13 per cent. in weight, corresponding to $2\frac{1}{2}H_2O$ (13·23 per cent.). On further heating to 110°, and subsequently to 160°, for a few minutes a further loss of 2·23 per cent. was experienced, corresponding approximately to $\frac{1}{2}H_2O$ (2·95 per cent.), and the total diminution in weight was thus 14·84 per cent. Indican dried in a vacuum, it was observed, had a behaviour which, as already indicated, supported the statements of Hoogewerff and ter Meulen, for it melted at about 100—101°, and remained in a fluid or semi-viscous condition after long heating to 110°. On cooling, it formed a brittle, vitreous mass containing no crystals. When subsequently heated to 160°, however, it rapidly became crystalline, although much discoloured, slight hydrolysis, no doubt, taking place at this temperature owing to the trace of water which was present. If indican dried in a vacuum is allowed to stand in moist air it approximately gains its original weight, as observed by Hoogewerff and ter Meulen, and this product, on now heating to 100°, quickly passes into the anhydrous crystalline condition.

As the purification of indican by means of water is far from economical, the following process, which succeeded better, was devised. The crude glucoside, containing water of crystallisation, was dissolved in about 3 parts of boiling absolute alcohol, the solution filtered, if necessary, by means of a vacuum, and while hot treated with boiling benzene to the point of turbidity. In case the liquid separated into two layers, a trace more alcohol was added, and the mixture allowed to cool. Small, colourless prisms soon commenced to separate, and the deposition was hastened by agitation, for otherwise the crystallisation was not complete for some hours. The product, after being collected and washed with benzene, melted sharply at 176—178°, and although possessing a faint pink colour was very nearly pure. The yield averaged 70 per cent., and a further quantity, although of inferior quality, separated from the mother liquors during distillation. A second treatment in a similar manner, employing animal charcoal, gave a colourless substance of extreme purity.

This method of purification was most useful when the glucoside was contaminated with traces of indigotin, for this, although readily removed by filtration when alcohol was used as the solvent, was not completely retained by the paper, and was a source of considerable trouble when aqueous solutions were employed.

The indican thus obtained was in the anhydrous condition, and differed considerably from the hydrated variety, being now somewhat sparingly soluble in boiling absolute alcohol and in acetone; from the former solvent it separated in colourless prisms. The production of this anhydrous form also occurs, although somewhat slowly, by digesting the hydrated glucoside with boiling absolute alcohol for a few minutes, and is deposited in this condition on cooling. Analysis of indican crystallised from benzene and alcohol gave:

$C = 57{\cdot}05$; $H = 6{\cdot}16$; $N = 4{\cdot}88$.

$C_{14}H_{17}O_6N$ requires $C = 56{\cdot}94$; $H = 5{\cdot}76$; $N = 4{\cdot}75$ per cent.

The general properties of the indican from the *Indigofera Sumatrana* are in agreement with those given by Hoogewerff and ter Meulen for their substance, so that the identity of the two products is evident, and no further description in this respect is necessary.

The fact that indican can be so readily isolated entirely without the aid of heat, and merely with the use of acetone, light petroleum, and ether,* is not in harmony with the contention of Schunck (*loc. cit.*), at all events in so far as the *Polygonum tinctorium* is concerned, that the crystalline glucoside is an alteration product of his amorphous indican, and consequently the terms *a*- and *b*-indican suggested by him should disappear. That Schunck obtained a concentrated form of indican from this plant cannot be doubted; moreover, the results he obtained so many years ago formed a valuable contribution to this important question.

The Analysis of Indican Solutions by Means of Isatin.—The fact that isatin condenses with indoxyl to form indirubin,

$$C_8H_7ON + C_8H_5O_2N = C_{16}H_{10}O_2N_2 + H_2O,$$

was, as is well known, discovered by Baeyer (*Ber.*, 1881, **14**, 1745), and this reaction has been employed both by Hazewinkel (*loc. cit.*) and by Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 120) for the characterisation of the indoxyl produced by the hydrolysis of indican. In the latter paper Beyerinck suggests that a quantitative indican determination may be based on this reaction, and as a result of this Orchardson, Wood, and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 4) have adopted such a method for the analysis of the indigotin-yielding content of the plant.† It was necessary therefore to determine by means of pure indican if the reaction is quantitative, and this was carried out in the manner described by these authors. Two distinct samples of indican were employed, (*a*) purified by crystallisation from water, and rendered anhydrous by drying, and (*b*) obtained in the anhydrous condition by means of benzene and alcohol.

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* The term "chemicals" employed by Schunck (*loc. cit.*) can hardly be taken to include the use of the sodium carbonate for the neutralisation of plant acid. On the other hand, crystalline indican can be isolated without adopting this precaution, but the yield is decreased by the formation of indigotin and brown products.

† The various leaf analyses given in this paper have been carried out by this process.

(*a*) 0·094 indican gave 0·083 indirubin. Theory requires 0·0835.
(*b*) 0·0992 „ 0·089 „ „ 0·0887.
(*b*) 0·0992 „ 0·0885 „ „ 0·0887.

The indirubin thus prepared was analysed.

Found C = 73·19; H = 4·02; N = 10·81.

$C_{16}H_{10}O_2N_2$ requires C = 73·28; H = 3·81; N = 10·69 per cent.

The reaction must therefore be considered as quantitative, and the suggestion of Beyerinck is thus confirmed.

Experiments on the persulphate method of analysis, originally devised by Rawson, and modified independently by Orchardson, Wood, and Bloxam (*loc. cit.*), and by Bergtheil (*J. Soc. Chem. Ind.*, 1906, **25**, 734), have more recently been carried out by Gaunt, Thomas, and Bloxam (*private communication*), employing pure indican. As a result, they were unable to obtain theoretical figures, and it accordingly appears that no method has yet been discovered by which a quantitative yield of indigotin can be obtained from this substance. Hazewinkel (*loc. cit.*) states, in regard to this point, that acid oxidising agents convert indican into indigo, and this in turn is oxidised by an excess of the reagent.

A very interesting result is obtained when nitrosodimethylaniline is employed as a source of oxygen, but the quantitative aspect of the process has not yet been determined. If indican dissolved in glacial acetic acid is treated with a small quantity of nitrosodimethylaniline no reaction appears to occur, but if a drop of hydrochloric acid be added and the mixture warmed, glistening leaflets of indigotin (Found N = 10·45) quickly separate. With the same reagents in aqueous solution, the indigotin is deposited in very minute crystals.

The Action of Acids on Indican.

It has been shown by Schunck and Römer (*loc. cit.*) that when their indican was exposed to acids in a vacuum, a compound was obtained which did not yield indigotin on oxidation, and in a previous communication (Trans., 1907, **91**, 295) such was shown to be the case when the leaf extract is boiled with acid in the absence of air. The product of the latter reaction was an amorphous brown substance, probably a mixture (found C = 66·04; H = 5·00; N = 5·67), and the clear filtrate from this on examination was shown to be free from indoxyl. These results suggested that the brown compound is in part derived from indoxyl, and the point is interesting in connexion with the origin of indigo-brown.

To obtain more definite information on this subject a preliminary examination of the behaviour of indican towards boiling dilute acids has been carried out. 4·06 grams of the glucoside in 100 c.c. of water were digested at the boiling point with 3 c.c. of sulphuric acid for one and a half hours, care being taken to exclude air. The liquid, at first yellow, soon became brown, a brown, resinous product, together with a little indigotin, soon separated, and the presence of indole was observed by means of its characteristic odour. Although the reaction proceeded rapidly at first, the last traces of indoxyl disappeared somewhat slowly, and as soon as this appeared to be absent, the mixture was cooled, and the insoluble matter collected and dried.

Curiously enough, this weighed 1·815 grams, for this was almost identical with the weight of indoxyl which would be liberated by the hydrolysis of the 4·04 grams of indican. An explanation is thus given of the brown precipitate referred to above, which is obtained by the digestion of an aqueous extract of *Indigofera* leaves with acid, although, as previously discussed, the low nitrogen content of this product is due either to its contamination with a non-nitrogenous compound of the same colour, or to the condensation of the indoxyl, or products thus derived from it, with some compound of this character present in the extract.*

The crude product of the reaction was extracted with boiling alcohol, by which means a small quantity (0·08 gram) remained undissolved; this consisted chiefly of indigotin, contaminated with a trace of a brown substance soluble in pyridine. The alcoholic extract, partly evaporated, was treated with ether, causing the precipitation of a brown amorphous compound, which was collected and washed with ether, and when dry weighed 0·65 gram. By evaporating the filtrate to a small bulk, and adding much ether, a further quantity, 0·25 gram, was isolated.

Analyses of this product, dried at 160°, gave:

$C = 68·10$; $H = 4·10$; $N = 9·34$ per cent.

It is sparingly soluble in alcohol, and when heated it is carbonised with evolution of a small quantity of yellowish-brown vapours, which condense to form an oil of the same colour. It is readily attacked by nitric acid, forming a deep brown liquid, and this, after standing for a short time, gives, with water, an orange-yellow amorphous precipitate.

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* The clear filtrate from this product contains a minute trace of an acid occurring in colourless needles, m. p. about 127—129°. This has not been yet identified and its connexion or otherwise with the indoxyl is uncertain.

It is remarkable that the percentage composition of this substance is almost identical with that which was ascribed by us to the main constituent of indigo-brown (*loc. cit.*):

$C = 68{\cdot}57$; $H = 4{\cdot}28$; $N = 10{\cdot}00$ per cent.,

and that the two products are very closely allied admits of but little doubt. From the very different circumstances which surround their formation, it could hardly be anticipated that they would prove to be identical, but, on the other hand, the differences appear to be but slight. The compound in question, for which the name *indoxyl-brown* is proposed, is more soluble in alcohol than the indigo-brown substance of the above composition, and in this respect resembles the more soluble and minor constituents of this product. With boiling dilute alkalis it is but little attacked, and its hot alcoholic solution on treatment with a drop of aqueous potassium hydroxide acquires a green tint. Unfortunately, no specimens of the more soluble indigo-brown compounds were available, so that at present it is impossible to say whether they also give this coloration. The production of brown compounds by Schunck (*loc. cit.*) from his indican, and the statement of Hazewinkel (*loc. cit.*) as to the behaviour of indoxyl in this respect, have already been dealt with in a former communication, and as experiments with pure indican have thus given a similar result, it is evident that this brown formation is a characteristic reaction of indoxyl.

The suspicion already discussed, that the presence of indigo-brown in natural indigo is due to the occurrence of a secondary reaction during the process of manufacture, becomes thus considerably strengthened, and results of more recent work at present incomplete have been most suggestive in this respect.

The Sugar.—The aqueous filtrate obtained during the formation of the indoxyl-brown was neutralised with barium carbonate, filtered, the clear liquid decolorised with animal charcoal and evaporated. The pale yellow, syrupy residue gave in the usual way, with phenylhydrazine, a voluminous, yellow precipitate, which was washed with a mixture of alcohol and chloroform and finally crystallised from alcohol. This compound melted at 204—205°, and was identical with glucosazone, so that the statement of Hazewinkel (*loc. cit.*), who, however, did not employ the crystalline glucoside, that indican, when hydrolysed, yields indoxyl and dextrose, is thus confirmed.

Indigofera arrecta.

As already indicated, it was possible by the method of Hoogewerff and ter Meulen to isolate indican from the leaves of this plant, and it was evident that this substance was identical with that present in the *I. Sumatrana* and *Polygonum tinctorium*. The *I. arrecta*, known as the Java or Natal plant, contains as a rule, in its leaf, a larger quantity of the glucoside than the ordinary Indian plant, a fact appreciated by the Dutch, and on this account, although somewhat late in the day, it is being experimented with in India for the manufacture of indigo.

Employing the acetone extraction process for the isolation of indican, satisfactory results have been obtained, but, on the other hand, the method does not proceed so well as with the *I. Sumatrana*. After evaporation of the acetone solution, treatment with light petroleum, solution in water, and removal of impurity by ether, the clear aqueous liquid containing the glucoside does not always yield crystals on evaporation in a vacuum. When this is the case, the viscous residue, dissolved in methyl alcohol, is treated with ether, to precipitate a colourless impurity; this is removed by decantation, the clear liquid evaporated, and the product dissolved in water and set aside to crystallise. Five hundred grams of the leaf (indigotin value = 0·865), extracted for five days in the cold with 2500 c.c. of acetone, gave 1·28 grams of the glucoside. An analysis of the substance, dried at 100°, gave:

$C = 56·83$; $H = 5·83$.

$C_{14}H_{17}O_6N$ requires $C = 56·94$; $H = 5·76$ per cent.

When crystallised from water, it melted at 57—58°, and in the anhydrous condition at 176—178°. The sugar yielded by the hydrolysis of this substance gave an osazone melting at 204—205°, which was glucosazone. The poor yield of indican obtained from this leaf, and the general difficulty of the process in regard to it, were found to be due to the presence of some quantity of a second soluble substance which hinders the crystallisation. To isolate this, the aqueous indican solution, after the ether treatment and partial evaporation, was again submitted to extraction with ether in a continuous apparatus for two days, by which means the indican was entirely removed by the ether, and could be partly recovered in the usual way. The residue obtained by the evaporation of the aqueous liquid was dissolved in methyl alcohol, and treated while hot with ether, which at first precipitated an amorphous product, but subsequently caused the deposition of crystals. These were collected and crystallised in a similar manner until colourless.

Found $C = 43·56$; $H = 7·44$.

$C_6H_{12}O_5$ requires $C = 43·90$; $H = 7·31$ per cent.

It consisted of colourless prisms readily soluble in water and alcohol, and as obtained above melted at 185—187°. This compound, which does not give an osazone, is reserved for further examination, and we hope shortly to have accumulated sufficient material for this purpose. In a private communication, Dr. F. B. Power, of the Wellcome Research Laboratories, suggests that this is possibly a modification of quercitol, for several of these are as yet unknown.

For the isolation of indican from the leaf, experiments have been made employing cold methyl alcohol as a solvent. This removes the glucoside more readily than acetone, for a sample of the *Indigofera arrecta* (indigotin value = 1·81), after digestion with six parts of the alcohol, had then an indigotin value of but 0·27 per cent. Unfortunately, however, numerous other impurities are thus dissolved which hinder the crystallisation of the indican, so that further work in this direction was abandoned.

Summary of Results.

The results of this investigation indicate that the indoxyl glucoside contained in the leaves of the *Indigofera Sumatrana* and *I. arrecta* is in both cases identical with the indican first isolated in a crystalline condition by Hoogewerff and ter Meulen from the *Indigofera leptostachya*, and from the *Polygonum tinctorium*. By employing acetone as a solvent for the glucoside, it is easy in the case of the *I. Sumatrana* to prepare rapidly large quantities of the pure substance, in amount equal to about 3 per cent. of the air-dried leaf. With the *I. arrecta*, the process, although effective, is not so simple, and this is caused chiefly by the presence of a sugar-like compound, $C_6H_{12}O_5$, possibly a modification of quercitol, which hinders the crystallisation. As the isolation of indican by this process can be carried out entirely without the aid of heat, and no chemicals are necessary, it is evident that the contention of Schunck, in so far as his work with the *Polygonum tinctorium* is concerned, that the crystalline indican is an alteration product of his own compound, cannot be upheld. As stated by Hoogewerff and ter Meulen, indican has the formula $C_{14}H_{17}O_6N$, crystallises from water with $3H_2O$, but its melting point in this condition is 57—58°, and not 51°, as is given in their paper; this is probably a clerical error. When heated to 100°, this product gradually solidifies, with production of the anhydrous substance which melts at 176—178°. When dried in a vacuum, indican, $C_{14}H_{17}O_6N,3H_2O$, melts at about 100—101°, as shown by the above chemists, and becomes crystalline only at a much higher temperature, with slight decomposition. Anhydrous indican is readily prepared by crystallising the hydrated variety from a mixture of benzene and alcohol, and is thus obtained in colourless prisms. Solutions of indican can, by means of isatin, be quantitatively estimated as indirubin, but, on the other hand, a theoretical yield of indigotin has not yet been produced by a combination of hydrolysis and oxidation.

On boiling indican with dilute acids, dextrose, as stated by Hazewinkel, is obtained, but the indoxyl liberated condenses with formation of brown amorphous products and with simultaneous production of a trace of indole. The main product of the reaction, and which is here termed indoxyl-brown, has a percentage composition almost identical with that of the main constituent of indigo-brown, which it very closely resembles. This point is advanced in further support of the opinion expressed in an earlier communication (*loc. cit.*), that indigo-brown is not only a derivative of indoxyl, but is also formed most probably as the result of a secondary reaction during the manufacture of indigo from the plant. A further study of this question, and other points which bear on the behaviour of indican, in circumstances allied to the actual manufacturing process on the large scale, are being investigated.

Experiments with the object of isolating the colouring principle of woad are in progress; the results at present obtained are in harmony with the statement of Beyerinck quoted in this paper.

Our thanks are due to Mr. F. Thomas for valuable help in connexion with the indirubin analyses given in this paper.

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Leeds.

CLXIII.—*The Relation between Viscosity and Chemical Constitution. Part I. The Viscosity of Pyridine Solutions.*

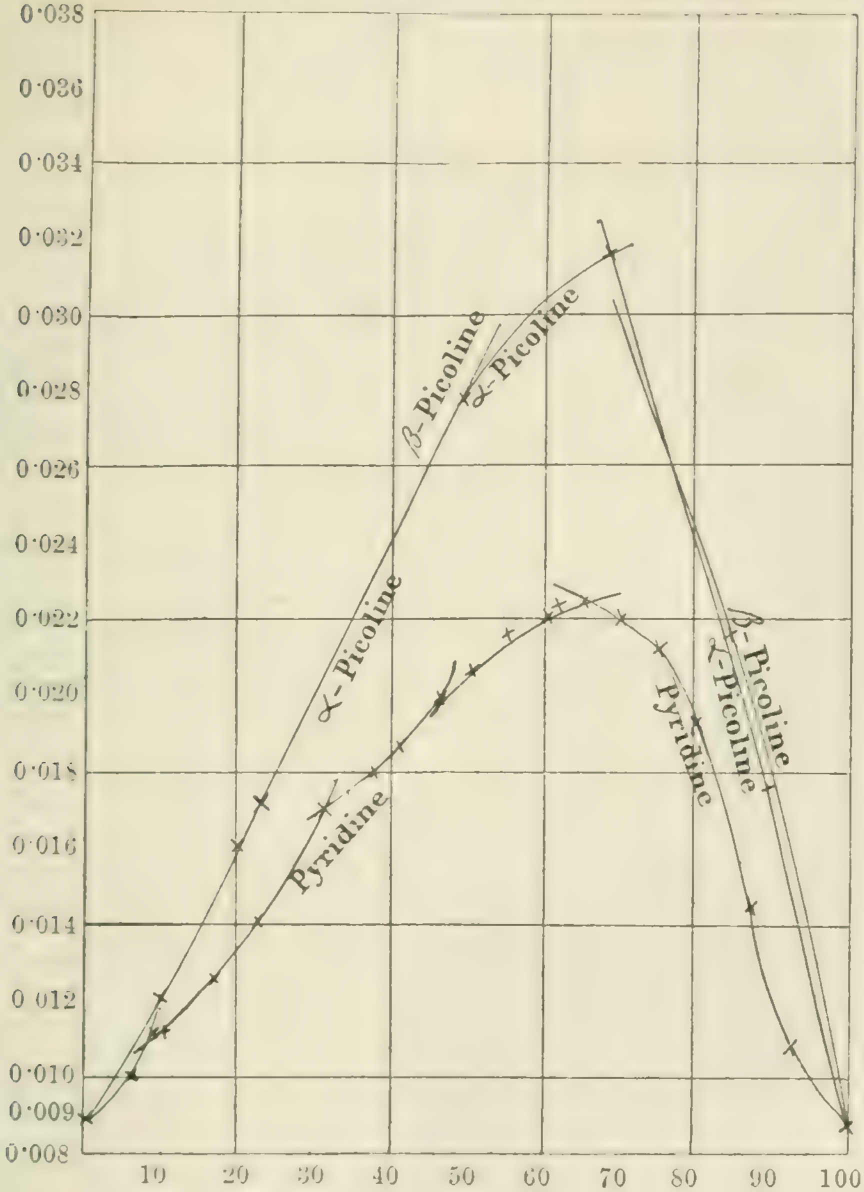
By Albert Ernest Dunstan, Ferdinand Bernard Theodore Thole, and John Samuel Hunt.

In this series of papers the authors desire to apply the results of the investigations on the viscosity of liquid mixtures (Dunstan, Trans., 1904, **85**, 817; 1905, **87**, 11; 1907, **91**, 83) to some special cases of constitution such as the well-known enol ketonic types of isomerism and the existence or not of racemates in solution.

In connexion with the former question, it was decided to use pyridine as a solvent for ethyl acetoacetate in the expectation of a furtherance of the isorropeic change, but preliminary experiments with this substance were of sufficient interest to justify a separate description of its behaviour in different solvents; moreover, the remarkable solvent power of pyridine, not only for organic but also for inorganic substances, makes a study of the viscosity-concentration curves afforded by its solutions of considerable importance.

FIG. 1.

Pyridine and picoline in water.



Innes (Trans., 1901, **79**, 261) showed that pyridine is a suitable solvent for hydroxylated compounds in the usual molecular weight determinations, and concluded that it had a dissociating effect. Von Laszczynski and von Gorski (*Zeitsch. Elektrochem.*, 1897, **4**, 299) found that solutions of many inorganic salts in pyridine have marked conductivity, and hence decided that it has an ionising influence, but Werner (*Zeitsch. anorg. Chem.*, 1897, **15**, 1), who used rather dilute solutions, found that normal molecular weights were obtained for many salts with the notable exceptions of mercuric iodide and cyanide. This led Jones (*Zeitsch. physikal. Chem.*, 1899, **31**, 114) to suggest the possibility of union between the dissolved salt and the solvent.

Pyridine has been examined in aqueous, benzene, and alcoholic solutions, α- and β-picoline in aqueous solution, and 2 : 6-lutidine in alcoholic solutions. The viscosity-concentration curves are shown in Figs. 1 and 2, whilst the density-concentration curves are illustrated in Fig. 3.

EXPERIMENTAL.

The materials used were supplied by Kahlbaum (pyridine and α-picoline) and Schuchardt (β-picoline and 2 : 6-lutidine). They were in each case distilled over potassium hydroxide before use. The apparatus employed was identical with that described in former papers, but the viscometer has been modified by the insertion of a graduated tap funnel fused on to the non-capillary side of the usual Ostwald-Poisseule instrument.

All observations were made at 25°, and weighings were corrected for displaced air only.

It is of interest to notice that this group of bases is extremely hygroscopic, that heat is evolved on dilution with water, and that solutions of the picolines in water tend to become discoloured on exposure to light.

Pyridine—Water.

Percentage of Pyridine.	Density $^{25}/_{4}$.	Viscosity.
0·00	0·99717	0·00891
5·85	0·99754	0·00934
9·11	0·99877	0·010997
9·85	0·99953	0·011097
15·33	1·00119	0·012460
22·55	1·00187	0·014027
30·99	1·00242	0·016916
37·06	1·00267	0·017886
40·46	1·00359	0·018630
50·03	1·00365	0·020515
55·12	1·00423	0·021472
59·98	1·00363	0·022004
61·46	1·00282	0·022155
64·99	1·00295	0·022438
70·03	1·00235	0·021913
75·01	1·00027	0·021151
79·80	0·99769	0·019201
87·96	0·99101	0·014424
94·96	0·98353	0·010810
100·00	0·97832	0·008775

It will be seen on referring to the curves that the effect of adding water to pyridine is to increase the viscosity to an extraordinary extent. The same effect is noticed when pyridine is added in increasing amount to water. Moreover, the curve obtained is not a smooth one; several discontinuities are to be observed. The maximum point lies at 65 per cent. of pyridine ($2C_5H_5N,5H_2O$ requires 63 per cent. of pyridine). The less important discontinuities are at 76 per cent. ($2C_5H_5N,3H_2O$ requires 74 per cent. of pyridine), 46 per cent. ($C_5H_5N,5H_2O$ requires 45·8 per cent. of pyridine), 32 per cent. ($C_5H_5N,10H_2O$ requires 30·5 per cent. of pyridine), and 9 per cent. (C_5H_5N,xH_2O where x is about 40) respectively of pyridine. As has been pointed out in previous communications, these discontinuities are located always at points of simple molecular concentrations. Moreover, it is well known that hydroxylated, associated liquids are comparatively highly viscous, and it has been laid down from the study of ample data that an increase in viscosity coefficient implies an increase in molecular mass, perhaps, to be more exact, in molecular volume.

Quite recently, Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405) have put forward the statement that such increase in viscosity is to be explained by dissociation, that is, by the proportionally larger frictional surfaces of smaller molecular masses. This contention, according to their view, is supported by the fact that minima on conductivity curves correspond with maxima on viscosity curves. Against this view, however, there is the well-known fact that maxima in viscosity curves correspond with aggregates of simple molecular composition, and that such aggregates have been actually isolated, also that heat effects and many other physical properties attain their maxima at the same points.

The argument as to larger frictional surfaces only holds good if it is definitely known that aggregated molecules are regular in shape and smooth in surface. Presumably an aggregated molecule would be more likely to cause friction than a congeries of simple molecules. The whole argument based on the effects of the larger or smaller "ionic volumes" of a solute on the viscosity of water fails for the same reason. There is no a priori evidence at hand for dogmatising as to the surfaces of ions.

It is noteworthy that the viscosity curves for α- and β-picoline are almost identical (Fig. 1). They attain, moreover, slightly different maxima, although both correspond approximately with $2C_6H_7N,5H_2O$ at 67 per cent. of α-picoline, and $C_6H_7N,2H_2O$ at 74 per cent. of β-picoline.

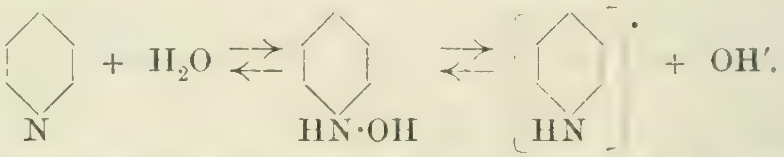
a-Picoline—Water.

Percentage of α-picoline.	Density $^{25}/_{4}$.	Viscosity.
0·00	0·99717	0·00891
10·28	0·99723	0·012066
23·05	0·99678	0·017106
49·51	0·99523	0·027789
68·67	0·98842	0·031656
89·59	0·96650	0·017362
100·00	0·94099	0·0079189

β-Picoline—Water.

Percentage of β-picoline.	Density $^{25}/_{4}$.	Viscosity.
0·00	0·99717	0·00891
10·00	0·99617	0·012024
19·80	0·98981	0·016042
68·55	0·98396	0·032912
88·71	0·96348	0·019717
100·00	0·93895	0·0087228

Hence the presence of a methyl group in the pyridine nucleus causes a greater affinity for water, but to about the same extent whether in the α- or β-position. Now the basicity of pyridine in aqueous solution is most probably due to the reactions expressed in the scheme:



The methyl group, then, furthers the attachment of water and assists the process from left to right. Certainly, wherever there is an atom capable of assuming a higher valency, there also is the tendency for association.

When pyridine is dissolved in benzene it furnishes a viscosity-concentration curve which is almost linear, indicating that neither component of the mixture exercises any marked effect on the other.

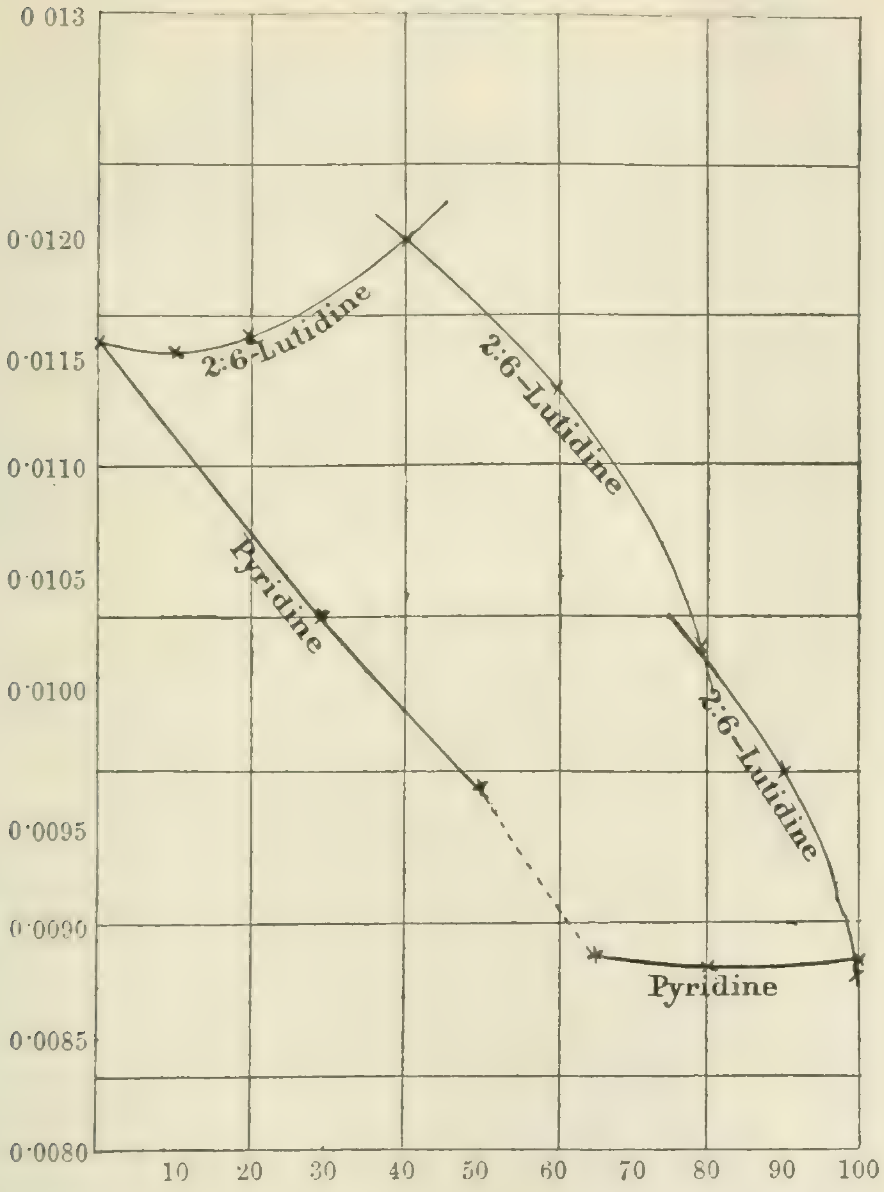
Pyridine—Benzene.

Percentage of pyridine.	Density $^{25}/_{4}$.	Viscosity.
0·00	0·87374	0·006038
39·73	0·91444	0·007169
59·35	0·93465	0·007726
79·64	0·95564	0·008345
89·77	0·96600	0·008601
100·00	0·97832	0·008775

Now we have reason to believe that both pyridine and benzene are associated, still, neither tends to dissociate the other. It is noteworthy that, although the molecular weights of pyridine and benzene are nearly identical, and the molecular volume of pyridine is less than that of benzene, yet pyridine is more viscous. This can be explained only by the view that pyridine is associated, and that to a higher extent than benzene. The presence of unsaturated nitrogen suffices to explain the association. At the same time, it is of interest to know that the viscosity of benzene itself is considerably higher than would

FIG. 2.

Pyridine and 2 : 6-lutidine in ethyl alcohol.



be expected from its molecular weight and that this is due undoubtedly to the latent unsaturation of its valencies.

A somewhat unexpected curve is given by solutions of pyridine in alcohol. It has been shown previously by one of the present authors that solutions of benzene and benzaldehyde in alcohol yield similar curves in which a minimum point is obtained. This minimum is to be explained by the dissociating action of the alcohol on the pyridine. A small amount of the notably more viscous alcohol depresses the viscosity coefficient of the pyridine, that is, separates the pyridine aggregates. The position of the minimum is at 80 per cent. of pyridine, which corresponds with $2C_5H_5N,1EtOH$. The remaining linear section of the curve appears to be the normal curve yielded by undissociated alcohol and dissociated pyridine. Hence, on producing this curve to the axis of viscosity we should obtain a value 0·0076 for the coefficient of the simple pyridine molecules.

Pyridine—Ethyl Alcohol.

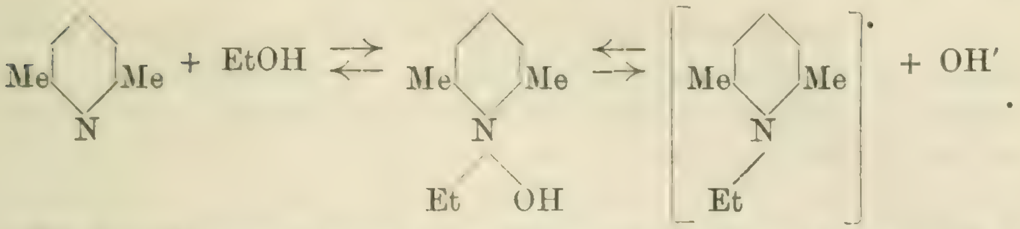
Percentage of pyridine.	Density $^{25}/_4$.	Viscosity.
0·00	0·79037	0·011532
29·92	0·84317	0·010340
49·97	0·88449	0·009591
66·07	0·92418	0·008792
79·96	0·94564	0·008773
100·00	0·97832	0·008775

It was not possible to investigate the viscosity-concentration curve afforded by 2 : 6-lutidine in aqueous solution owing to its sparing solubility. In alcohol, however, a somewhat complex curve results (Fig. 2), the interpretation of which is difficult. Lutidine apparently at first dissociates alcohol, for a minimum point is observable at 12 per cent. of lutidine, then the viscosity increases, and a maximum is reached at 40 per cent.

2 : 6-*Lutidine—Ethyl Alcohol.*

Percentage of 2 : 6-lutidine.	Density $^{25}/_4$.	Viscosity.
0·00	0·79043	0·011536
9·97	0·80382	0·011499
19·88	0·81972	0·011643
39·77	0·85145	0·012023
59·70	0·88029	0·011328
79·43	0·90743	0·010204
90·55	0·92101	0·009686
100·00	0·93218	0·0087766

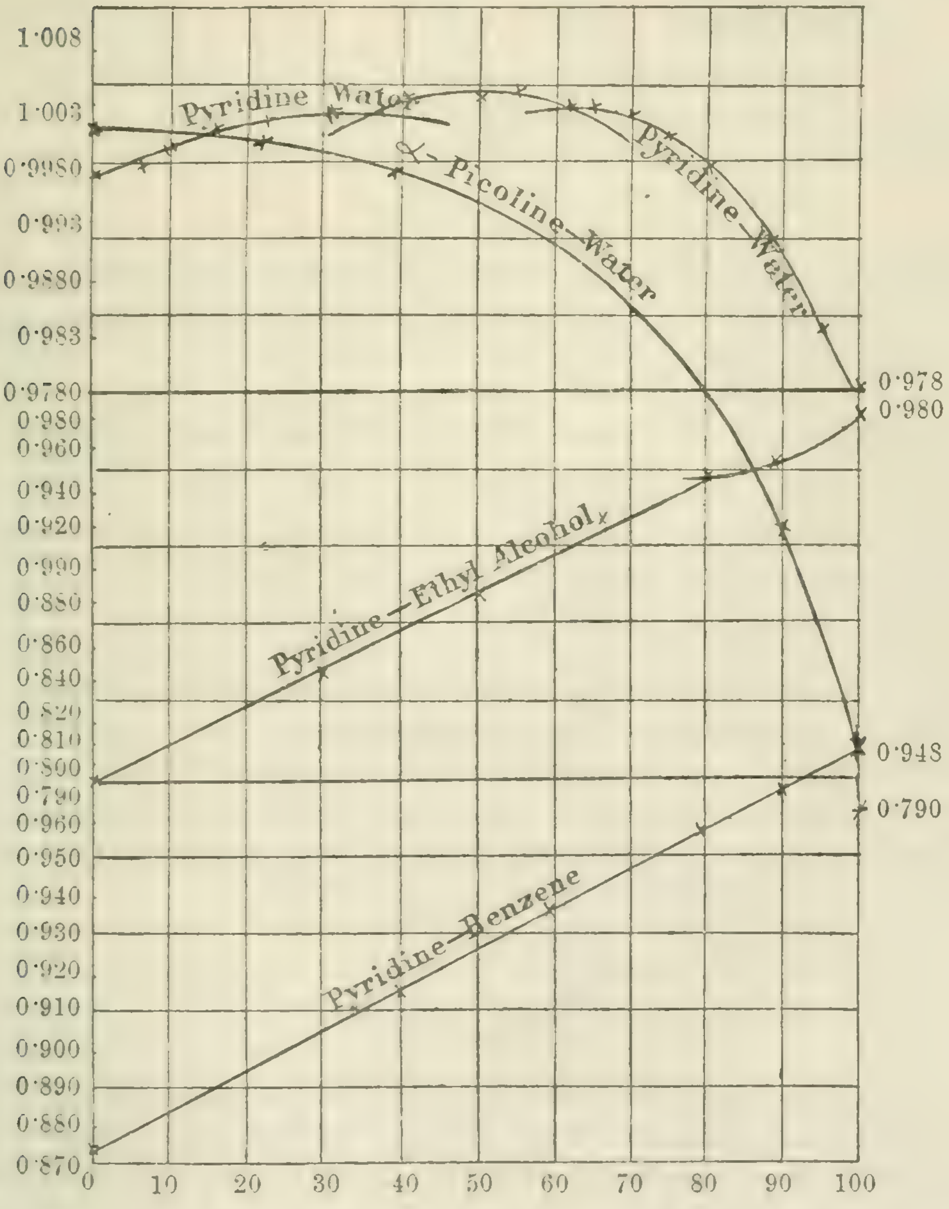
Beyond this point, with the exception of a minor discontinuity at 80 per cent., this curve does not depart very much from a straight line. The maximum is attained at a concentration represented by $C_6H_7N,3EtOH$. The presence of the methyl radicle in the diortho-position with respect to the nitrogen profoundly modifies the behaviour of the substance, inasmuch as it confers upon the nitrogen atom the capacity of attaching alcohol to itself in a manner analogous to that in which pyridine unites with water.



The density-concentration curves furnished by the mixtures in this state are shown in Fig. 3. They call for very little comment.

FIG. 3.

Density—concentration.



Mainly they are quite normal in nature, being smooth curves from end to end. The β-picoline-water curve follows, very nearly, the same course as that of α-picoline, the corresponding values being smaller. The discontinuities in the pyridine-water density curve correspond approximately with those on the viscosity curve. Very similar discontinuities are to be found on the density and viscosity curves for alcohol-pyridine.

The authors desire to thank Prof. Trouton for his kind interest in this investigation, and to express their gratitude to the Research Fund Committee of the Chemical Society for a grant, which has covered the cost of the materials.

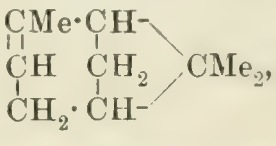
University College,
East Ham Technical College.

CLXIV.—*Experiments on the Synthesis of the Terpenes. Part XI. Synthesis of* 4-iso*Propylidene*cyclo*hexanone and its Derivatives.*

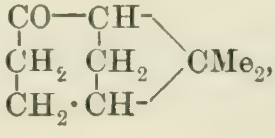
By William Henry Perkin, jun., and John Lionel Simonsen.

The synthetical experiments which have been carried out in the terpene series have, so far, led only to the synthesis of those terpenes which, like dipentene, contain a single closed chain.

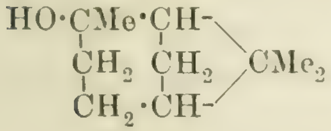
It is, however, characteristic of this series that some of its most important members belong to the bicyclic system, and, for a long time, we have been engaged on experiments instituted with the object of devising means for the synthesis of such terpenes. The problem appears to be one of unusual experimental difficulty, not only on account of the fact that there are very few methods available for the formation of bicyclic or bridged ring compounds, but also because the bridge in such terpenes as pinene,

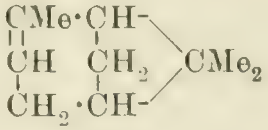


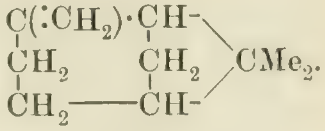
is so unstable, especially towards acids, that the reagents available for synthetical work are more strictly limited than is usually the case. The present communication contains an account of an attempt to synthesise nopinone,



a ketone of great interest which Baeyer (*Ber.*, 1896, **29**, 22, 25) first obtained during the course of his classical researches on the oxidation of oil of turpentine. It was thought that this ketone would probably react with magnesium methyl iodide to yield an alcohol (methylnopinol) which, when treated with dehydrating agents, would be decomposed with elimination of water and formation either of pinene or ψ-pinene:


Methylnopinol.


Pinene.


ψ-Pinene.

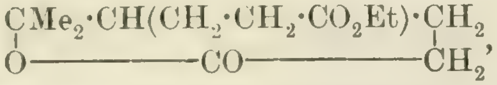
We therefore prepared a quantity of nopinone and found that it reacted normally with magnesium methyl iodide, and the methylnopinol produced proved to be a crystalline substance melting at 58°.

While engaged in the investigation of the action of various dehydrating agents on this tertiary alcohol, Prof. O. Wallach informed us that he had, for some time, been studying this decomposition,* and we have therefore discontinued our work on this part of the subject. The experiments which we have carried out in our attempt to synthesise nopinone may be briefly summarised as follows.

The sodium derivative of ethyl α-acetylglutarate,

$$CO_2Et{\cdot}CAcNa{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et,$$

was treated, in alcoholic solution, with ethyl β-iodopropionate, when interaction rapidly took place with the formation of *ethyl γ acetylpentane-αγε tricarboxylate*, $CO_2Et{\cdot}CAc(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, and this ester, when digested with hydrochloric acid, was readily decomposed and converted into *γ-acetylpimelic acid*, $CHAc(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$. When ethyl γ-acetylpimelate is treated with magnesium methyl iodide, it is converted into the *lactone* of *ethyl hydrogen* γ-iso*propenolpimelate*,



$$\begin{array}{l}CMe_2{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et){\cdot}CH_2\\ |\qquad\qquad\qquad\qquad\qquad\qquad\quad |\\ O\text{————}CO\text{————}CH_2,\end{array}$$

and this lactone reacts readily with hydrobromic acid with formation of an oil which, on esterification, yields ethyl γ-(*bromo*iso*propyl*) *pimelate*, $CMe_2Br{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$.

When this bromo-ester is digested with pyridine, it is decomposed with elimination of hydrogen bromide and formation of ethyl γ-iso*propylidenepimelate*, $CMe_2{:}C(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, which distils at 168° (13 mm.) and, on hydrolysis, yields γ-iso*propylidenepimelic acid* (m. p. 97°), the constitution of which is proved by the fact that, on oxidation with permanganate and then with chromic acid, it yields acetone and succinic acid. The solution of ethyl γ-*iso*propylidenepimelate in toluene reacts readily with sodium and yields *ethyl* 4-iso*propylidene*cyclo*hexanone-2-carboxylate*,

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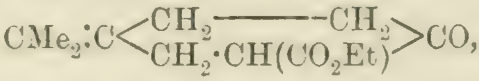
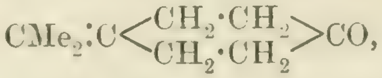
* A preliminary account of these experiments has lately appeared in the *Nachr. k. Ges. Wiss. Göttingen*, 1907, p. 13; see also *Annalen*, 1907, **356**, 239.



$$CMe_2{:}C<\begin{matrix}CH_2\text{———}CH_2\\ CH_2{\cdot}CH(CO_2Et)\end{matrix}>CO,$$

an oil which decomposes on distillation and the alcoholic solution of which gives an intense violet coloration with ferric chloride.

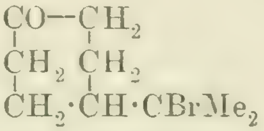
This ketonic ester is readily hydrolysed by alcoholic potash, and one of the products of hydrolysis is 4-iso*propylidene*cyclo*hexanone*,



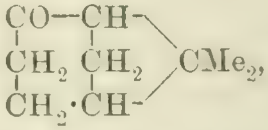
$$CMe_2{:}C<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}>CO,$$

which distils at 219—221°, yields a *semicarbazone* of melting point 201°, and is isomeric with nopinone (b. p. 210°), camphenilone (b. p. 195°), sabineneketone (b. p. 213°), and with other important ketones of the camphor and terpene series (compare p. 1746).

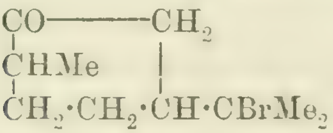
4-*iso*Propylidene*cyclo*hexanone combines readily with hydrogen bromide with formation of 4-*β-bromo*iso*propyl*cyclo*hexanone*,[*] and if the formula of this substance is written side by side with that of nopinone,



and



it will be, at once, seen that these substances are related in the same way as dihydrocarvone hydrobromide to carone:



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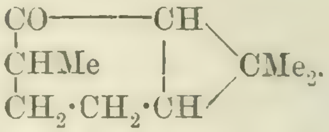

Now Baeyer (*Ber.*, 1894, **27**, 1919; 1896, **29**, 6) has shown that carone is formed when dihydrocarvone hydrobromide is left in contact with alcoholic potash at 0°, and, in order to bring about the similar conversion of 4-β-bromo*iso*propyl*cyclo*hexanone into nopinone, we

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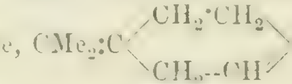
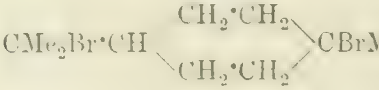
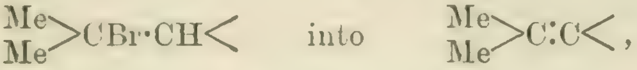
[*] That this hydrobromide contains the grouping $CMe_2Br{\cdot}CH<$ and not $CMe_2H{\cdot}CBr<$ is proved by comparison with other analogous cases of the addition of hydrogen bromide to the grouping $CMe_2{:}C<$.

Terpinolene,  $CMe_2{:}C<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2\text{--}CH\end{matrix}>C{\cdot}Me$, for example, yields dipentene dihydrobromide,  $CMe_2Br{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}>CBrMe$, when it is treated with hydrobromic acid.

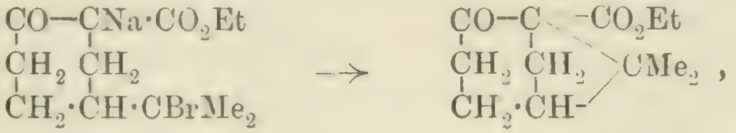
caused this bromo-compound to react with alcoholic potash under a variety of conditions, but were unable to detect the formation even of traces of nopinone. In every case, the elimination of hydrogen bromide appeared to proceed principally in the direction:



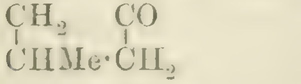
$$\mathrm{Me_2{>}CBr{\cdot}CH{<}}\quad\text{into}\quad\mathrm{Me_2{>}C{:}C{<}},$$

giving rise to the formation of 4-*iso*propylidene*cyclo*hexanone.

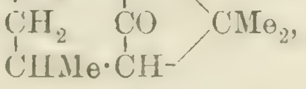
We next prepared the hydrogen bromide additive compound of ethyl 4-*iso*propylidene*cyclo*hexanone-2-carboxylate (see p. 1745), a substance capable of yielding a sodium derivative which might reasonably be expected readily to undergo internal condensation with elimination of sodium bromide and formation of ethyl nopinonecarboxylate:



but, although elimination of sodium bromide did take place when the sodium derivative was digested in alcoholic solution, the product of the reaction, on hydrolysis with dilute alcoholic potash, did not furnish a trace of nopinone. In a previous communication (Trans., 1907, **85**, 817), we had occasion to refer to the fact that the *cyclo*propane ring is not infrequently produced with much greater ease than the *cyclo*butane ring. Obviously the inability of the four-carbon chain to close under the highly favourable conditions presented in the case of the sodium derivative of ethyl 4-β-bromo*iso*propyl*cyclo*hexanone-2-carboxylate, whereas the formation of the *cyclo*propane ring takes place with such remarkable ease in the conversion of dihydrocarvone hydrobromide into carone, is strong evidence that, in a bicyclic system, the *cyclo*propane ring is more readily produced than the *cyclo*butane ring. Another example in illustration of this point is afforded by the behaviour of the hydrobromide of pulegone (I),



(I.)



(II.)

which, when treated with alcoholic potash, is reconverted into pulegone and does not yield a bicyclic ketone (II) of the type of nopinone.

Ethyl α-Acetylglutarate, $CO_2Et{\cdot}CHAc{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, *and Ethyl γ-Acetylpentane-αγε-tricarboxylate*, $CO_2Et{\cdot}CAc(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$.

Ethyl α-acetylglutarate has already been described by Wolff (*Annalen*, 1883, **216**, 129) and by Bentley and Perkin (Trans., 1896, **69**, 1511), and the following modified method was adopted as most convenient for the preparation of the large quantities of this ester which were required for the present research.

Sodium (11·6 grams) is dissolved in alcohol (150 grams), well cooled, and mixed with ethyl acetoacetate (65 grams), ethyl β-iodopropionate (114 grams) is then slowly added, care being taken that the temperature does not rise above 30° either during addition or for some hours afterwards. After twelve hours, the product is heated on the water-bath for half an hour, diluted with water, extracted with ether, and the ethereal solution washed thoroughly with water, dried over calcium chloride, and evaporated. On fractionation under reduced pressure (17 mm.), much ethyl acetoacetate passes over first, then nearly pure ethyl α-acetylglutarate (78 grams) distils at 158—165°, and almost the whole of the residue distils at 210—220° and consists of *ethyl γ-acetylpentane-αγε-tricarboxylate.*

The formation of the latter substance and the regeneration of a corresponding amount of ethyl acetoacetate is readily understood from the equation:

$$2CHAcNa{\cdot}CO_2Et + 2CH_2I{\cdot}CH_2{\cdot}CO_2Et = \\ CH_2Ac{\cdot}CO_2Et + CHAc(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2 + 2NaI.$$

A large amount of this valuable ester was obtained in this way, and further large quantities were prepared by the following process.

Sodium (11·5 grams) is dissolved in alcohol (150 grams), mixed with ethyl α-acetylglutarate (115 grams), and ethyl β-iodopropionate (114 grams) gradually added, any rise of temperature above 30° being avoided by cooling under the tap. After standing for twelve hours, the product is heated on the water-bath for half an hour, diluted with water, and the oil extracted with ether, washed with water, and dried in the usual manner. With the exception of a considerable quantity of ethyl acrylate (formed by the elimination of hydrogen iodide from some of the ethyl β-iodopropionate employed), the product of the reaction distils almost constantly at 217° (15 mm.), and consists of *ethyl γ-acetylpentane-αγε-tricarboxylate*:

0·1483 gave 0·3156 CO_2 and 0·1055 H_2O. C = 58·0; H = 7·9.

$C_{16}H_{26}O_7$ requires C = 58·2; H = 7·9 per cent.

This ester, which does not appear to have previously been prepared, is a viscid, colourless oil and possesses only a faint odour.

γ-Acetylpimelic Acid, $CHAc(CH_2\cdot CH_2\cdot CO_2H)_2$.

This acid is readily obtained when ethyl γ-acetylpentane-αγε-tricarboxylate is hydrolysed by hydrochloric acid. The ester (68 grams) is digested in a reflux apparatus with concentrated hydrochloric acid (136 grams) for eight hours, water (150 c.c.) is then added, and the boiling continued for a further eight hours. When the product is evaporated on the water-bath, γ-acetylpimelic acid remains as a thick syrup which (like so many derivatives of pimelic acid) shows no tendency to crystallise. A small quantity was purified by conversion into the semicarbazone (see below) and subsequent regeneration by decomposition with hydrochloric acid, and, after remaining over sulphuric acid in an evacuated desiccator, the almost colourless syrup gave the following approximate results on analysis:

0·1808 gave 0·3461 CO_2 and 0·1111 H_2O. C = 52·2; H = 6·8.
$C_9H_{14}O_5$ requires C = 53·5; H = 6·9 per cent.

The basicity of the acid was determined by titration with decinormal potassium hydroxide, when 0·1377 neutralised 0·0751 KOH, whereas this amount of a dibasic acid, $C_9H_{14}O_5$, requires 0·0763 KOH for neutralisation.

The *semicarbazone* is obtained when the acid is treated with semicarbazide hydrochloride and sodium acetate in the usual manner, and separates from hot water in plates which melt at 177°:

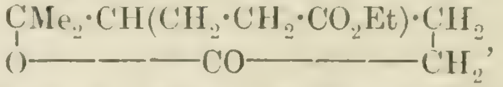
0·1961 gave 26·2 c.c. of nitrogen at 14° and 767 mm. N = 15·9.
$C_{10}H_{17}O_5N_3$ requires N = 16·2 per cent.

Ethyl γ-Acetylpimelate, $CHAc(CH_2\cdot CH_2\cdot CO_2Et)_2$.—This ester is obtained when the solution of the crude acid (150 grams) in 3 per cent. alcoholic hydrogen chloride (300 c.c.) is allowed to stand for thirty-six hours. On pouring into water, a heavy oil separates, which is extracted with ether, the ethereal solution is washed with dilute sodium carbonate, dried over calcium chloride, evaporated, and the ester purified by fractionation under reduced pressure:

0·1649 gave 0·3619 CO_2 and 0·1257 H_2O. C = 59·8; H = 8·5.
$C_{13}H_{22}O_5$ requires C = 60·5; H = 8·5 per cent.

Ethyl γ-acetylpimelate distils at 186—192° (14 mm.) and has a pleasant ethereal odour.

*The Lactone of Ethyl Hydrogen γ-*iso*Propenolpimelate,*



$$\begin{array}{l}\mathrm{CMe_2{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et){\cdot}CH_2} \\ \mathrm{O{-\!-\!-\!-}CO{-\!-\!-\!-}CH_2}\end{array},$$

*and its Conversion into Ethyl γ-(Bromo*iso*propyl)pimelate,*

$CMe_2Br{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$.

In preparing the lactone, ethyl γ-acetylpimelate (50 grams), dissolved in ether (300 c.c.), was slowly added to a well cooled ethereal solution of magnesium methyl iodide (prepared from 9·4 grams of magnesium), when an extremely vigorous action took place and a large quantity of a white magnesium compound separated.

After remaining overnight, the magnesium compound was decomposed by dilute hydrochloride acid in the usual manner, when nearly the whole of the lactone remained in the ethereal solution. This was well washed with sodium sulphite to remove iodine, dried over calcium chloride, evaporated, and the resulting oil fractionated under reduced pressure (22 mm.), when the main portion distilled at about 200°:

0·1987 gave 0·4603 CO_2 and 0·1522 H_2O. C = 63·2; H = 8·5.

$C_{12}H_{20}O_4$ requires C = 63·2; H = 8·8 per cent.

The *lactone* of *ethyl hydrogen γ-*iso*propenolpimelate* is a colourless oil possessing a pleasant odour of camphor.

*Ethyl hydrogen γ-(bromo*iso*propyl)pimelate* is obtained when the lactone is dissolved in five times its weight of a solution of hydrogen bromide in glacial acetic acid (saturated at 0°) and allowed to stand for twenty-four hours. On pouring into water, a heavy oil separates, which is extracted with ether, and the ethereal solution, after thoroughly washing with water to remove acetic and hydrobromic acids, is dried over calcium chloride and the ether evaporated.

A small quantity of the oil, after remaining over sulphuric acid in an evacuated desiccator for some days, gave the following approximate results on analysis:

0·2257 gave 0·1308 AgBr. Br = 24·7

$C_{12}H_{21}O_4Br$ requires Br 25·9 per cent.

*Ethyl γ-(Bromo*iso*propyl)pimelate*, $CMe_2Br{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$.—In preparing this ester, ethyl hydrogen γ-(bromo*iso*propyl)pimelate (50 grams) was dissolved in 15 per cent. alcoholic hydrogen chloride (100 c.c.) and allowed to stand for twenty-four hours. The oil, which separated on dilution with water, was extracted with ether, the ethereal solution washed with sodium carbonate, dried over calcium chloride, and evaporated, when the residual, viscid, brown oil, after remaining for some days over sulphuric acid in an evacuated desiccator, had decomposed somewhat with evolution of hydrogen bromide, and therefore gave only approximate results on analysis.

γ-iso*Propylidenepimelic Acid*, $CMe_2:C(CH_2\cdot CH_2\cdot CO_2H)_2$, *and its Ethyl Ester.*

Ethyl γ-iso*propylidenepimelate* is obtained when ethyl γ-(bromo*iso*-propyl)pimelate is digested for four hours on the water-bath with five times its volume of anhydrous pyridine, during which operation quantities of pyridine hydrobromide separate. The product is cooled, acidified with dilute hydrochloride acid and extracted with ether, the ethereal solution is well washed, dried over calcium chloride, evaporated, and the ester purified by distillation under reduced pressure :

0·1624 gave 0·3917 CO_2 and 0·1398 H_2O. C = 65·8 ; H = 9·6.
$C_{14}H_{24}O_4$ requires C = 65·6 ; H = 9·4 per cent.

Ethyl γ-iso*propylidenepimelate* distils at 168° (13 mm.) and has a faint odour of peppermint. The free acid is obtained when the ester is digested with an excess of methyl-alcoholic potash on the water-bath for half an hour. After diluting with water, the solution is evaporated until quite free from methyl alcohol, cooled, acidified with dilute hydrochloric acid, and the acid extracted with pure ether. The ethereal solution is dried over calcium chloride and evaporated, when a colourless syrup is obtained which soon almost completely crystallises, and, after remaining in contact with porous porcelain until quite free from oily impurity, the acid was finally purified by crystallisation from pure dry ether :

0·1326 gave 0·2919 CO_2 and 0·0981 H_2O. C = 60·0 ; H = 8·2.
$C_{10}H_{16}O_4$ requires C = 60·0 ; H = 8·0 per cent.

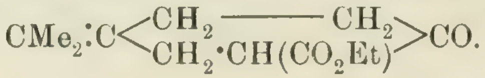
γ-iso*Propylidenepimelic acid* melts at about 97° and is readily soluble in ether, chloroform, or ethyl acetate, but sparingly so in water or light petroleum. Its solution in sodium carbonate instantly reduces permanganate, but when dissolved in chloroform the acid does not decolorise bromine. The basicity of the acid was determined by titration with decinormal sodium hydroxide, when 0·0557 neutralised 0·0022 NaOH, whereas this amount of a dibasic acid, $C_{10}H_{16}O_4$, should neutralise 0·0022 NaOH.

Oxidation of γ-iso*Propylidenepimelic Acid to Acetone and Succinic Acid.*—In carrying out this oxidation, the acid (3 grams) was dissolved in dilute sodium carbonate and oxidised at 0°, in an apparatus fitted with a turbine, with dilute permanganate until the colour just remained. The slight excess of permanganate was removed by the addition of sodium sulphite, and the filtrate and washings of the manganese precipitate evaporated to a small bulk, transferred to an ordinary distilling flask, and, after heating to boiling, a strong solution of potassium dichromate and sulphuric acid added until no further action took place. On the addition of *p*-bromophenylhydrazine acetate to the distillate, a copious precipitate separated which, after collecting and drying on porous porcelain, melted at 95—97° and consisted of acetone-*p*-bromophenylhydrazone.

The residue in the distillation flask was saturated with ammonium sulphate and extracted with ether, when the ethereal solution, after drying over calcium chloride and evaporating, deposited a solid acid which was recrystallised from water. It separated in colourless plates, melted at 185°, and consisted of succinic acid:

0·1343 gave 0·1995 CO_2 and 0·0650 H_2O. C = 40·5; H = 5·3.
$C_4H_6O_4$ requires C = 40·7; H = 5·1 per cent.

Action of Sodium on Ethyl γ-iso*Propylidenepimelate. Formation of Ethyl* 4-iso*Propylidene*cyclo*hexanone-2-carboxylate*,



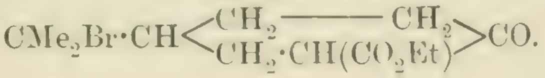
$$CMe_2{:}C\Big\langle\begin{matrix}CH_2 \text{———————} CH_2\\ CH_2\cdot CH(CO_2Et)\end{matrix}\Big\rangle CO.$$

In carrying out this condensation, sodium (5 grams) is melted under boiling toluene, shaken vigorously in order to bring it into as fine a state as possible, and, after cooling, ethyl γ-*iso*propylidenepimelate (28 grams) is added, and the whole heated in an oil-bath at 110—120° until decomposition commences. A vigorous action ensues, and is controlled by removing the flask from the oil-bath from time to time, and, finally, the process is completed by heating for two to three hours at 110—120°, when practically the whole of the sodium will have disappeared. After cooling, the sodium derivative is cautiously decomposed by adding ice-water and dilute hydrochloric acid and the product extracted with ether. The ethereal solution is well washed with dilute sodium carbonate, dried over calcium chloride, and the ether distilled off; the toluene is then removed as far as possible by distillation under reduced pressure. The residual oil, which decomposes considerably even when distilled under 15 mm. pressure, could not be obtained quite free from toluene, and gave therefore only approximate results on analysis:

0·1312 gave 0·3416 CO_2 and 0·1012 H_2O. C = 71·0; H = 8·6.
$C_{12}H_{18}O_3$ requires C = 68·6; H = 8·6 per cent.

Ethyl 4-iso*propylidene*cyclo*hexanone-2-carboxylate* has a pleasant odour somewhat resembling that of ethyl acetoacetate, and gives, in alcoholic solution, a deep violet coloration on the addition of ferric chloride.

Ethyl 4-*β-Bromo*iso*propyl*cyclo*hexanone-2-carboxylate*,



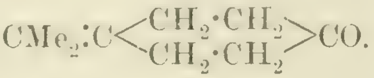
$$\mathrm{CMe_2Br\cdot CH}<\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CH_2\cdot CH(CO_2Et)}\end{matrix}>\mathrm{CO}.$$

Ethyl 4-*iso*propylidene*cyclo*hexanone-2-carboxylate dissolves readily in a solution of hydrogen bromide in glacial acetic acid (saturated at 0°) with little evolution of heat, and if, after standing for an hour and a half, water is added, the addition product is precipitated as a heavy oil. This was extracted with ether, the ethereal solution washed with water and sodium carbonate, and evaporated, when a thick, brown oil was obtained which, after remaining over sulphuric acid in an evacuated desiccator for twenty-four hours, gave the following results on analysis:

0·2607 gave 0·1722 AgBr. Br = 28·1.

$C_{12}H_{19}O_3Br$ requires Br = 27·5 per cent.

4-iso*Propylidene*cyclo*hexanone*,



$$\mathrm{CMe_2{:}C}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CO}.$$

The preparation of this ketone from ethyl 4-*iso*propylidene*cyclo*hexanone-2-carboxylate by hydrolysis is a matter of considerable difficulty, and the yield is always poor. After many comparative experiments, the following process was thought to give the best results.

The keto-ester (12 grams) is mixed with a cold solution of potassium hydroxide (7 grams) in methyl alcohol (100 c.c.) and, after remaining for twenty-four hours, heated on the water-bath in a reflux apparatus for two hours, during which operation a quantity of potassium carbonate separates. The product is diluted with water and distilled in steam, when the readily volatile ketone rapidly passes over.*

After saturating with ammonium sulphate, the distillate is extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure:

0·1350 gave 0·3865 CO_2 and 0·1304 H_2O. C = 78·1; H = 10·7.

$C_9H_{14}O$ requires C = 78·2; H = 10·1 per cent.

4-iso*Propylidene*cyclo*hexanone* distils at about 160° under 100 mm., and at 219—221° under 749 mm., pressure; it is a colourless, mobile oil and possesses the pleasant odour characteristic of cyclic ketones.

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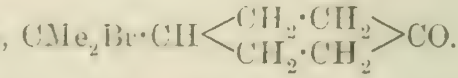
* The residue in the distillation flask contains unchanged keto-ester, and, after extraction with ether and treatment with alcoholic potash, yields a further small quantity of ketone.

The *semicarbazone* separates rapidly when the ketone is shaken with an excess of a concentrated solution of semicarbazide hydrochloride and sodium acetate. It crystallises from methyl alcohol in prismatic needles and melts at 201° with decomposition:

0·2089 gave 38·5 c.c. of nitrogen at 12° and 757 mm. N = 21·7.

$C_{10}H_{17}ON_3$ requires N = 21·5 per cent.

4·β-*Bromo*iso*propyl*cyclo*hexanone*,



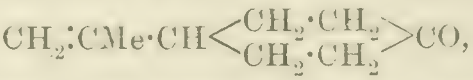
$$\mathrm{CMe_2Br\cdot CH}{<}^{\mathrm{CH_2\cdot CH_2}}_{\mathrm{CH_2\cdot CH_2}}{>}\mathrm{CO.}$$

This substance is readily obtained when the pure ketone is dissolved in five times its volume of a solution of hydrogen bromide in glacial acetic acid (saturated at 0°). After remaining for half an hour, the addition product is precipitated by water, the heavy oil extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, and evaporated, when a viscid oil is obtained which has a strong odour of peppermint and becomes brown on exposure to the air:

0·1486 gave 0·1289 AgBr. Br = 36·9.

$C_9H_{15}OBr$ requires Br = 36·5 per cent.

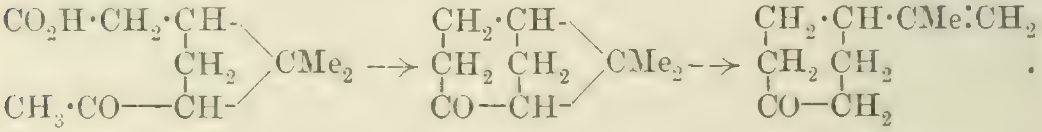
4-*iso*Propylidene*cyclo*hexanone is isomeric with, and closely allied to, 4-*iso*propenyl*cyclo*hexanone (iso*propenyl*-p-*ketohexamethylene*),



$$\mathrm{CH_2{:}CMe\cdot CH}{<}^{\mathrm{CH_2\cdot CH_2}}_{\mathrm{CH_2\cdot CH_2}}{>}\mathrm{CO,}$$

which had previously been obtained in small quantities by one of us (Trans., 1904, **85**, 670)* during the course of experiments on the action of magnesium methyl iodide on ethyl *cyclo*hexane-4-carboxylate.

A ketone, which is probably identical with 4-*iso*propenyl*cyclo*hexanone, has also been described by Semmler (*Ber.*, 1904, **37**, 239) under the name *pinophorone*. It was prepared by the distillation of the calcium salt of crude pinonic acid, a decomposition which Semmler formulates thus:



Pinonic acid. Intermediate ketone. Pinophorone.

The intermediate product (nopinone) is assumed to be unstable at the high temperature necessary for the decomposition of the calcium salt and to undergo isomeric change with formation of pinophorone.

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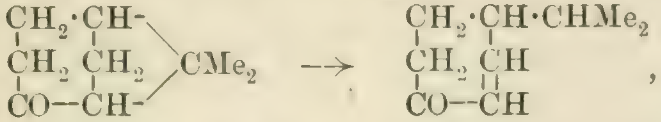
* By an unfortunate mistake, the boiling point of 4-*iso*propenyl*cyclo*hexanone was given as 184—186° under the ordinary pressure, whereas the distillation was actually carried out under a pressure of 300 mm.

Quite recently, Wallach (*Nachr. k. Ges. Wiss. Göttingen*, 1907, p. 10; *Annalen*, 1907, **356**, 235) has shown that the bridge in nopinone very readily undergoes fission when this ketone is boiled with dilute sulphuric acid, and the 4-iso*propyl*-Δ^2-cyclo*hexenone*,

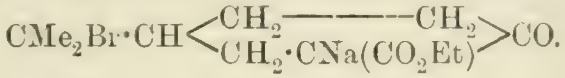


thus obtained, and which distils at 220—224°, is again isomeric with the 4-*iso*propylidene*cyclo*hexanone described in the present communication.

Attempts to Synthesise Nopinone.

It is explained in the introduction that the object of the present research was the synthesis of nopinone, and the following are some of the experiments which were made in the hope of accomplishing this important synthesis.

I. *The Decomposition of the Sodium Derivative of Ethyl* 4-*β-Bromo*iso*propyl*cyclo*hexanone-2-carboxylate,*



$$CMe_2Br\cdot CH\left<\begin{matrix}CH_2\text{———————}CH_2\\CH_2\cdot CNa(CO_2Et)\end{matrix}\right>CO.$$

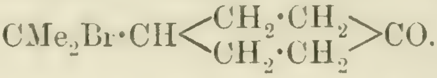
In this experiment, an alcoholic solution of the bromo-ester (4·1 grams) was added to a cold solution of sodium (0·32 gram) in alcohol and, since no decomposition appeared to take place after remaining at the ordinary temperature for three hours, the solution was heated on the water-bath in a reflux apparatus, when sodium bromide rapidly separated. The product was diluted with water, the ester extracted with ether, hydrolysed with alcoholic potash (compare p. 1745), and then distilled in steam, when a small quantity of a ketone was obtained which yielded a semicarbazone of melting point 191° with decomposition. That this was not the semicarbazone of nopinone (m. p. 188°) was proved by mixing equal quantities of the two specimens, when the mixture melted at about 157°. On the other hand, when mixed with the semicarbazone of 4-*iso*propylidene*cyclo*hexanone (m. p. 201°), the mixture melted at about 195°, indicating that this ketone had been produced in the above experiment.

II. *The Action of Alcoholic Potash on Ethyl* 4-*β-Bromo*iso*propyl*cyclo*hexanone-2-carboxylate.*

This experiment was carried out under the conditions employed by Baeyer (*Ber.*, 1894, **27**, 1919) in his experiments on the conversion of dihydrocarvone hydrobromide into carone. The bromo-ester (36 grams) was dissolved in alcohol, cooled to −10° in ice and salt, and then alcoholic potash (8 grams KOH) added drop by drop, any rise of temperature being carefully avoided. After remaining overnight in the ice-chest, it was found that much potassium bromide had separated.

The product was cooled to −5°, mixed again with the same quantity of alcoholic potash, and, after twenty-four hours, the solution was boiled for two hours in a reflux apparatus with the gradual addition of alcoholic potash (KOH = 5 grams). After dilution with water and distillation in steam, an oil was obtained which contained 4-*iso*propylidene*cyclo*hexanone and the careful investigation of which failed to indicate the presence even of traces of nopinone.

III. *The Action of Alcoholic Potash on 4-β-Bromo*iso*propyl*cyclo*hexanone*,



$$CMe_2Br{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CO.$$

This experiment need not be described in detail, since the conditions were very similar to those employed in experiment II.

The product consisted mainly of 4-*iso*propylidene*cyclo*hexanone and did not appear to contain nopinone.

One of the principal difficulties which we had to deal with in the above experiments was the impossibility of obtaining ethyl 4-*iso*propylidene*cyclo*hexanone-2-carboxylate, and especially 4-*iso*propylidene*cyclo*hexanone, in sufficient quantity for detailed investigation. Owing to the very large quantities of ethyl β-iodopropionate required, the preparation of these substances is very costly, and, in spite of a large number of comparative experiments, the yield was always very small. Possibly, when better methods of preparation are available, it may still be found possible to carry out a synthesis of nopinone on the lines indicated above.

We are greatly indebted to the Royal Society and to the Chemical Society for grants which have covered much of the heavy expense of this investigation.

THE SCHUNCK LABORATORY,
THE UNIVERSITY,
MANCHESTER.

FARADAY LECTURE.

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on Friday, October 18th, 1907.)

Synthetical Chemistry in its Relation to Biology.

By Emil Fischer, F.R.S.

Exactly forty years are elapsed since Faraday's death and already, on eight occasions, discourses in honour of his memory have been delivered, at the instance of this Society, by distinguished representatives of the sciences which he did so much to forward. Most of them, mindful of Faraday's discoveries, have dealt with general problems connected with our fundamental conceptions of matter and its inherent forces, so that, when honoured with the invitation to deliver the ninth of these lectures, I could not but feel sensible of the difficulty of following the example of my predecessors, as the field in which I have sought to enlarge the boundaries of knowledge is one far removed from such considerations.

In Faraday's time, it is true, the labours of workers in the natural sciences were not specialised as they are now; his genius was such, however, that he was able, although not trained in its service, to enrich organic chemistry with observations of momentous consequence. I need but allude to his discovery of benzene: the practical importance of this substance and its dominant position in the host of carbon compounds with which we are acquainted were generally recognised in the course of the celebration held in this room, only fifteen months ago, in honour of Sir William Perkin.

But in the course of his labours as an investigator Faraday never approached the attractive problems which organic chemistry affords on its biological side. I must therefore crave your indulgence in selecting this theme in particular as the subject of my address. Happily, I am sustained by the conviction that biology, on account of the breadth and importance of its aims, may claim to rank with the inorganic sciences, although perhaps it lacks their exactness of method; nowhere can it count on fuller recognition of its achievements and of the importance of its problems than among the countrymen of Charles Darwin.

It is easy to understand why in its early youth organic chemistry was so closely connected with biology; the materials which the chemist was called upon to investigate were mostly products of animal or vegetable origin. Indeed, carbohydrates, proteins and vegetable acids served Lavoisier, Gay-Lussac, Berzelius and Liebig as materials in elaborating the methods of elementary analysis.

The isolation of urea from animal urine by Rouelle, the recognition of uric acid, lactic acid, malic acid and glycerine by Scheele, the isolation of asparagine by Vauquelin and Robiquet, of morphine by Serturnier, together with many other similar discoveries accomplished during the first ten years of the nineteenth century, are admirable examples of the manner in which the living world was drawn upon and made to yield up its treasure of chemical compounds. The many hundreds of natural organic compounds enumerated in the text-books of animal and vegetable chemistry are proof of the rich harvest since gathered in this field of investigation. But how small is their number when compared with the 130,000 carbon compounds which organic chemistry can boast of to-day. All these, it is known, are either products of the artificial transformation of organic matters occurring naturally or have been completely synthesised from their elements. The accumulation of this huge material, including the elaboration of the necessary methods, has been the main occupation of organic chemists during the past sixty years; and as their discoveries gave rise to much happy speculation, they often took the lead in developing chemical theory.

It is not to be denied that, in the latter half of the last century, owing to the growth of the subject in importance, organic chemistry became separated from biology. It cannot be mere chance that the most famous of Liebig's pupils, A. W. Hofmann, A. Kekulé and A. Wurtz, did not follow the example of their great teacher, whose chief triumphs were won by the use he made of chemical methods in solving biological problems. Perhaps they were restrained by the feeling that, mainly through his influence, physiological chemistry had been developed into a separate discipline, which should be cared for by men who could devote themselves entirely to its service. Such subdivision of labour undoubtedly has many advantages; the disadvantages would have outweighed these had it precluded interchange of experiences and friendly co-operation of workers in the two fields; the history of both sciences, however, affords ample proof that such has not been the case.

Physiologists have ever been ready to avail themselves of the latest developments of chemical analysis and synthesis, whilst organic chemists have not only been stimulated in many ways by biologists but their studies have derived much practical aid from biological science. I may instance the modern development of the chemistry of fermentation, which began with the pioneer work of Pasteur and was greatly favoured by the introduction of refined bacteriological methods by Koch and Hansen; also the flourishing industry to which the manufacture of medical remedies prepared by synthetic methods has given rise.

But organic chemistry will certainly never be content to act as the mere handmaid of biology. This is impossible, as the theoretical and technical problems which she is called upon to consider are already numerous and they cannot fail to increase in number and importance in the future. But I do consider it not only possible but desirable, that the close connexion of chemistry with biology which prevailed in the days of Liebig and Dumas should be re-established, as the great chemical secrets of life are only to be unveiled by co-operative work. I will therefore attempt to indicate the part chemistry can play by reference to cases of which I can claim to have personal experience.

We know that in nature the construction of organic matter begins in the leaves of plants with the conversion of carbon dioxide into sugar, from which many physiologists suppose the complex substances contained in the living cell are formed by further changes in which nitrogen, sulphur and phosphorus take part.

These transformations are for the most part enveloped in mystery. We know nothing definitely even of the assimilation of carbon dioxide. Of the various hypotheses advanced to explain the change, that advocated by A. von Baeyer has gained most support, namely, the view that the initial product is formaldehyde, glucose being formed from this by a process of polymerisation. Actually both changes have been effected by artificial means. After it had been shown by Butleroff that a sugar-like, syrupy product is formed on heating formaldehyde with lime water and O. Loew had improved the method of effecting the condensation, I was able to adduce proof that the complex mixture contains a small quantity of α-acrose which can be transformed into glucose. The preparation of glucose from carbon dioxide thus became a possibility, as it was known that carbon dioxide could be converted into formaldehyde by more or less drastic processes. Recently, Fenton has succeeded in carrying out the reduction of carbon dioxide to formaldehyde at a low temperature in aqueous solution, so that it is now possible to effect the complete synthesis of sugar at temperatures such as prevail in the living plant. But how thorough is the work of the plant in comparison with our laboratory practice; usually when such questions are discussed, the poor yields which our methods give rise to are forgotten!

I need only allude here to recent apparently successful attempts, on the one hand, to effect the reduction of carbonic acid to formaldehyde by means of light and, on the other, to detect formaldehyde in green leaves, as Professor Meldola dealt exhaustively and critically with these questions in his Presidential Address eighteen months ago. I may be allowed, however, to dwell somewhat on one peculiar feature of the natural change, namely, the asymmetric character of the synthesis; according to present knowledge—I may refer especially to the brilliant investigations of H. Brown and Morris—the optically active hexoses of the *d*-series, glucose and fructose, are alone formed.

But from the experience gained in effecting syntheses in the sugar group, as I showed some time ago, it is possible to give a fairly satisfactory explanation of this change. It is only necessary to assume that the condensation is preceded by the formation of an additive compound of formaldehyde with some optically active constituent of the chlorophyll granules. I shall give a more precise form to this hypothesis if I say that I consider it probable that the carbon dioxide itself enters into combination in this manner, as there is reason to suppose that the proteins offer sufficient opportunity for its fixation; according to Siegfried, even the simple amino-acids are capable of combining with carbon dioxide. I am inclined to think that this compound with carbon dioxide undergoes decomposition into oxygen and a reduction product, probably a derivative of formaldehyde; the condensation to sugar takes place either in the original asymmetric complex or in one produced from it by a secondary change involving the separation of the formaldehyde and its re-association in some other manner. It may be that the condensation takes place directly or that intermediate compounds, biose or glycerose, are formed. Thanks to the researches of Marckwald and especially those of Mackenzie, we are acquainted with a whole series of asymmetric syntheses; no one of these, however, is half so complete as that involved in the formation of sugar under natural conditions. Indeed, it is obvious that if the natural process is to be imitated *in vitro*, it will be necessary to alter the methods hitherto adopted in every single detail; difficult as this may appear, it is not altogether impossible.

But even if this be done successfully, the precise nature of the assimilation process will not be finally elucidated. It is to be expected that this will only be accomplished when biological research, aided by improved analytical methods, has succeeded in following the changes which take place in the actual chlorophyll granules.

The carbohydrates elaborated by the plant undergo combustion to carbon dioxide and water in the animal body. The change is easily effected by means of powerful oxidising agents at the ordinary temperature; the natural process, however, must be a very different one, as in the organism oxygen is conveyed to the carbohydrate by oxidising enzymes and doubtless many intermediate products are formed of which we know little at present.

It would be easy to multiply examples. But these two are sufficient to demonstrate the incompleteness of the explanation of biochemical processes deduced from the data of organic chemistry. The service rendered to biology by chemical analysis and synthesis—which will be rendered to it in even greater measure in the future—is to be sought in other directions.

The ultimate aim of biochemistry is to gain complete insight into the unending series of changes which attend plant and animal metabolism. To accomplish a task of such magnitude, complete knowledge is required of each individual chemical substance occurring in the cycle of changes and of analytical methods which will permit of its recognition under conditions such as exist in the living organism. As a matter of course, it is the office of organic chemistry, especially of synthetic chemistry, to accumulate this absolutely essential material. The chemical constitution of hundreds of carbon compounds which occur naturally has already been determined and their more important properties have been established. But far more remains to be done. In proof of this, let me briefly direct your attention to the three great classes of substances which predominate in the living world: the fats, the carbohydrates and the proteins.

It was established at least ninety years ago by Chevreul, in the course of his celebrated investigations into the process of soap-making, that the fats can be decomposed into the glycerine discovered by Scheele and into fatty acids; but the relationship of these latter to one another could not be understood until the conception of homologous series had been evolved in organic chemistry. The classical researches of Berthelot and the discovery of glycol by Wurtz were necessary preliminaries to the establishment of the constitution of glycerine; the final proof that the fats are neutral glyceric salts of the fatty acids was first provided by Berthelot's synthesis. Synthetic methods have made us acquainted with the mono- and di-glycerides and also with mixed triglycerides such as have frequently been met with of late in nature.

Nevertheless, the group in which the natural fats are ranged is one in which there are still many gaps and many misstatements to be corrected. Fatty acids of high molecular weight, which for years were regarded as entities, such as margaric acid, are now acknowledged to be mixtures; others, like the cerotic acid of beeswax, have received new formulæ; in fact, the higher acids and the oxy-acids all require to be studied afresh and, whilst it is true that the general constitution of the fats is known with certainty and the quantitative composition of the most important natural mixtures is established with a fairly satisfactory degree of accuracy, yet there is much uncertainty on the physiological side; even such an apparently simple problem as that involved in the determination of the manner in which fats are absorbed in the animal intestine has not yet been definitely solved. Although enzymes capable of cleaving fats are known to be present in the secretions of the stomach and pancreas, opinions are still divided as to whether the fat is absorbed in a state of fine emulsion or whether it first undergoes hydrolysis.

Still less is known of the manner in which fats undergo combustion to carbon dioxide and water in the animal body. Hitherto this change has been imitated artificially only at relatively high temperatures. It is obvious that it would be of far greater interest to discover oxidising agents which would produce the effect at low temperatures. No doubt many intermediate products would be met with and the study of these would afford valuable assistance to biologists in devising experiments with animals.

The formation of fats in plant and animal tissue is no less complicated a phenomenon. It is certain that carbohydrates are the chief source of supply. We know next to nothing, however, of the actual course of this remarkable synthesis; it is easy to imagine that glycerol may be formed by the hydrolysis of glucose and that three molecules of glucose may give rise to an acid containing eighteen carbon atoms. But the process involved in the conversion of sugar which is rich in oxygen into fatty acids containing little oxygen remains wrapped in mystery. I imagine that this change, like that which attends alcoholic fermentation, is effected by a rearrangement of oxygen atoms within the molecule and that it involves the elimination of carbon dioxide. To imitate such a process artificially, of course, is an attractive problem to be dealt with from the synthetic side; but it is doubtful if it can ever be solved by purely chemical methods. In all probability, the organism has at its disposal for the purpose a number of enzymes which effect the complete synthesis in a series of interactions following rapidly one upon another.

The problems afforded by the fats are simple, however, in comparison with those connected with the carbohydrates. The original subdivision of the group into mono-, di-, tri- and poly-saccharides has been justified in practice. Up to the present time only the monosaccharides have been studied satisfactorily from the point of view of their spatial structure. The dogma which at one time prevailed that Nature produces only carbohydrates with six atoms of carbon was upset by Kiliani's discovery that arabinose contains but five atoms of carbon. Since then the group of the monosaccharides has been so extended by synthetic means that sugars of all types, from glycollaldehyde (biose) to the nonoses, are now known, the group including besides the seven compounds which occur naturally no less than forty-five synthesised products.

Our knowledge of this group is also fairly satisfactory from the stereochemical standpoint, as the greater number of the isomerides predicted by theory as well as the more important aldohexoses and aldopentoses have been prepared and their inter-relationship can be expressed by steric formulæ. Similar results have been arrived at in the case of the great class of glucosides, the synthesis of the most simple representative from glucose and methyl alcohol having led to the discovery of both the theoretically possible stereoisomerides.

The growth of our knowledge of the monosaccharides has proved in many ways to be of importance in connexion with biological inquiry, especially in enabling us to penetrate the mystery of enzyme action somewhat further.

On contrasting the effects which emulsin and the enzymes in yeast produce on the various glucosides prepared by synthetic methods, I was led to conclude not only that there was a difference between the two series of optical antipodes similar to that discovered by Pasteur in the course of his studies of moulds but that very slight changes in configuration were sufficient to inhibit the action of enzymes entirely. I was led by these observations to apply the simile of *lock* and *key* as an expression of the close inter-relationship in configuration which obtains between the enzyme and the substance which it attacks.

Similar results were obtained on investigating the behaviour of the stereoisomeric hexoses with yeast, the fermentative power of which we now attribute to an enzyme: E. Buchner's zymase.

The experience gained with the glucosides became of service in studying the polysaccharides; for example, maltose and milk sugar were found to differ in their behaviour towards the enzymes of yeast and emulsin much as do α- and β-methylglucoside. Another outcome of the investigation has been the discovery of distinct enzymes capable of attacking di- and tri-saccharides. Thus lactase was found to be present in Kefir grains and milk sugar yeasts and definite proof was given of the presence of a maltase in beer yeast. As the result of these inquiries, I was able to formulate a rule of general biological significance, namely, that the alcoholic fermentation of a polysaccharide is necessarily preceded by its hydrolysis by some particular enzyme. It was shown, especially in the case of the invertase of *Monilia Candida*, that it is not essential that the enzyme should even be soluble in water. I may mention here that E. Buchner has himself admitted that he was led by these observations on *Monilia* to make his experiments on the mechanical separation of zymase from the yeast cell.

Unfortunately but few successful syntheses of polysaccharides have been effected. Musculus obtained dextrin-like products from grape sugar by treating it with mineral acids; and I have shown that a disaccharide, *iso*maltose, may be produced in this way. E. Frankland Armstrong and I have prepared a number of disaccharides by synthesis from the acetylchlorohydroses; one of these products, probably, is identical with melibiose.

But methods such as I refer to are so difficult in their application that their use cannot well be extended to any large number of polysaccharides. It is most desirable therefore that better methods should be devised, as it is probable that the attack on the dextrins, gums and similar undeciphered substances is most likely to be successful if made from the synthetic side. It is to be expected that biology would gain much by the discovery and utilisation of such materials; more, perhaps, than it has from the study of the monosaccharides and of the glucosides prepared by artificial means.

The carbohydrate group is that in which use was first made of enzymes as synthetic agents. You are aware that Croft Hill succeeded in preparing complex carbohydrates by subjecting glucose to the action of the enzymes in beer yeast. His contention that the product is maltose has been controverted; it is more probable that the condensation which glucose undergoes under the influence of the enzyme resembles that effected by hydrogen chloride, that is to say, that the product is a mixture of *iso*maltose with nonfermentable dextrins. In any case, Croft Hill has the great merit of having been the first to demonstrate the reversibility of enzyme action and since his experiments were made similar results have been obtained with other enzymes, lipase, for example.

An important extension of Croft Hill's discovery is afforded by E. F. Armstrong's observation that the action of emulsin is different from that of the enzymes of yeast, the condensation of glucose taking place in such a way that a disaccharide which appears to be maltose is formed together with other complex products. Such syntheses effected by the agency of enzymes fascinate the imagination, as they approximate closely to natural processes; but I may point out that they cannot take the place of purely chemical methods, as these latter are so much more under our control and can be varied in so many ways that we are in the position to produce materials which it is quite impossible for the organised world to furnish. Laboratory synthetic methods will be indispensable for a long time to come, not only for preparative purposes but also as the means of elucidating the structure of complex substances of natural origin.

This contention is applicable to the proteins even more than it is to the carbohydrates: as they are among the most complex substances produced in the living world and are concerned in all the vital activities of the cell, a complete comprehension of their nature must obviously precede the full development of biological chemistry. I may therefore be allowed to give very briefly a rapid survey of the present position of the chemistry of the proteins. The investigation necessarily began with the isolation and classification of the natural materials; and these were subdivided according to purely external characteristics, such as origin, solubility, coagulability and the like. On the basis of such properties, we distinguish to-day some forty to fifty natural proteins, discovered by the joint labours of chemists and physiologists; but it is to be expected that as the methods of differentiating and separating them are improved, their number will be largely increased.

At present the majority are known only in an amorphous form; some important terms of the group, however, such as oxyhæmoglobin, egg albumin and the albumin of horse serum, excelsin from the Brazil nut and the edestins from other plant seeds have been obtained in definite crystals. But, unfortunately, it cannot be decided from their crystalline appearance whether these products are definite substances, as the tendency to form mixed crystals is the greater the more complicated the molecule. Examples in point are afforded by the aniline dyes, the higher fatty acids and the purine compounds; and those who have studied the chemistry of the natural silicates will be aware of the extension which mineralogists have been compelled to give to the conception of isomorphism. It would therefore be altogether surprising if the crystallised natural proteins should turn out to be single substances. In this gathering of expert chemists I need not dwell on the difficulties to which this uncertainty gives rise.

Of the numerous attempts to unravel the constitution of the proteins by analytical means, the only method which has given useful results hitherto is that of hydrolysis. Hydrolysis can be effected by acids or by alkalis and also by digestive enzymes; the products, it is well known, besides ammonia, are albumoses, peptones and ultimately amino-acids. The wide range of variation in composition of these amino-acids is illustrated in the following table:

Glycine (Braconnot, 1820).
Alanine (Schützenberger, Weyl, 1888).
Valine (v. Gorup-Besanez, 1856).
Leucine (Proust, 1818; Braconnot, 1820).
*iso*Leucine (F. Ehrlich, 1903).

Phenylalanine (E. Schulze and Barbieri, 1881).

Serine (Cramer, 1865).
Tyrosine (Liebig, 1846).

Aspartic acid (Plisson, 1827).
Glutamic acid (Ritthausen, 1866).

Proline (E. Fischer, 1901).
Oxyproline (E. Fischer, 1902).

Ornithine (M. Jaffé, 1877).
Lysine (E. Drechsel, 1889).
Arginine (E. Schulze and E. Steiger, 1886).

Histidine (A. Kossel, 1896).
Tryptophane (Hopkins and Cole, 1901).

Diaminotrihydroxydodecanoic acid (E. Fischer and E. Abderhalden, Skraup, 1904).
Cystine (Wollaston, 1810; K. A. H. Mörner, 1899).

In this table are included all the substances hitherto prepared from the proteins the existence of which is established, with a short reference to their discovery. It may, however, be mentioned that the list is by no means complete; among the new products already announced, the caseanic acid described by Skraup appears to have the greatest claim to recognition as a definite substance. It is certain, however, that the nineteen amino-acids in the table are the chief hydrolytic cleavage products of the proteins and those which are most generally met with. Their discovery has been made during a period of eighty four years, but no less than five of them have been recognised within the present century.

The proportions in which the various amino-acids are obtained from the different proteins vary very considerably. In some cases they are altogether lacking, as may be proved by application of the definite tests for tyrosine, tryptophane or glycine; but it is worthy of note that, as a rule, the amino-acids referred to as isolated from the mixtures produced by subjecting albuminous substances to hydrolysis all occur almost without exception: especially is this true of the important proteins which play the chief part in animal or vegetable metabolism: so that the conclusion must be drawn that none of them can be dispensed with in organic life. With the exception of diaminotrihydroxydodecanoic acid, they have all been so thoroughly investigated that their structure is well established. The majority also have been synthesised, proof of their structure having, in fact, been given in this way. Only oxyproline, histidine and diaminotrihydroxydodecanoic acid remain still to be synthesised.

With the exception of glycine, all the amino-acids derived from natural sources are optically active; but when prepared by ordinary synthetic methods, as is well known, they are obtained in the first instance in the racemic form. The resolution of the racemoids into their optically active components has been effected quite recently in most cases. Asparagine, however, which is closely related to aspartic acid, had been resolved into the two active forms by recrystallising the inactive synthetic product from water and separating the two constituents mechanically. Moreover, in the case of some other amino-acids, for example, leucine, the antipode of the natural form had been obtained by partially fermenting the synthetic product with moulds. The complete synthesis of the active amino-acids which are obtained from natural sources was first accomplished by the method I introduced based upon the use of the acyl derivatives. The method has been applied with success to the majority of the synthetic products; its extension to the remaining cases, proline, lysine, tryptophane and cystine, is not likely to be attended with any difficulties. The synthetical results are summarised in the following table, in which the inactive products are marked *dl* and the natural active products are recorded separately:

Glycine (Perkin and Duppa, 1858).
Alanine *dl*- (A. Strecker, 1850).
,, *d*- (E. Fischer, 1899).
Valine *dl*- (Fittig and Clark, 1866).
,, *d*- (Fischer, 1906).
Leucine *dl*- (Limpricht, 1855; E. Schulze and Likiernik, 1885).
Leucine *l*- (Fischer, 1900).
*iso*Leucine *dl*- (Bouveault and Loquin, 1905).
*iso*Leucine *d*- (Loquin, 1907).
Phenylalanine *dl*- (Erlenmeyer and Lipp, 1883).
Phenylalanine *l*- (Fischer and Schöller, 1907).
Serine *dl*- (Fischer and Leuchs, 1902).
,, *l*- (Fischer and Jacobs, 1906).
Tyrosine *dl*- (Erlenmeyer and Lipp, 1883).
,, *l*- (Fischer, 1900).
Aspartic acid *dl*- (Dessaignes, 1850).
,, ,, *l*- (Piutti, 1887).
Glutamic acid *dl*- (L. Wolff, 1890).
,, ,, *d*- (Fischer, 1899).
Proline *dl*- (R. Willstätter, 1900).
Ornithine *dl*- (Fischer, 1900).
,, *d*- (Sörensen, 1905).
Arginine, active; partial synthesis from ornithine (E. Schulze and Winterstein, 1899).
Lysine *dl*- (Fischer and Weigert, 1902).
Tryptophane *dl*- (A. Ellinger and Flamand, 1907).
Cystine *dl*- (Erlenmeyer, jun., 1903).

I have been able to refer the configuration of some of these substances to that of glucose. This correlation was first effected thirteen years ago in the case of aspartic acid. As you are aware, this acid is converted by nitrous acid into *l*-malic acid, the configuration of which can be deduced from its relationship to tartaric acid. In a similar manner, it has been found possible recently to connect serine and alanine with active glyceric acid, which Neuberg and Silbermann have been able to correlate with tartaric acid and which it may be anticipated will also be obtained directly from the tetroses by adopting methods such as those introduced by Wohl and Ruff. It will probably be found that the method is applicable to most of the other amino-acids, so that it is to be expected that at no distant date a uniform steric system will be established which will include all the optically active substances in the sugar group, the hydroxy-acids and the amino-acids.

It is not without purpose that I have dwelt so long on what appear to be side issues of synthetic work, for I firmly believe that they will prove in many respects to be of service to biological inquiry. In proof of this, reference may be made to several cases in which they have already borne fruit. For example, the proof given by E. Schulze and Winterstein that arginine is a derivative of guanidine and, therefore, also of urea had undoubtedly some influence in stimulating H. Kossel to the discovery of the interesting manner in which this amino-acid is resolved into urea and ornithine by means of liver arginase.

To test the assumption that ornithine and lysine are carboxylic acids of tetra- and penta-methylenediamines, Ellinger subjected these substances to the action of putrefactive bacteria and was successful in converting them into the well known basic products of putrefaction.

The manner in which taurine is formed in the animal body has been made clear by Friedmann's proof of the relation between cystine and taurine.

The isolation of tryptophane by Hopkins and Cole and its conversion into scatole enable us to form a clear picture of the manner in which this offensive substance is produced by intestinal putrefaction and to indicate also the origin of the indoxylsulphuric acid discovered by E. Baumann in urine and of the indigo-blue which is sometimes met with in this secretion. I need do no more than point out, however, that this connexion could not possibly have been established had not A. von Baeyer laid the foundation by his great synthetic achievements in the indigo group.

The discovery of *iso*leucine and its relationship to leucine led F. Ehrlich, a few years ago, to undertake his interesting experiments on the conversion of amino-acids into primary alcohols by means of beer yeast, which enabled him to give the long-sought explanation of the formation of fusel oil during alcoholic fermentation.

Such instances will be multiplied rapidly in the future; considerations of the relationship of the natural amino-acids to various other classes of substance from the structural and stereochemical point of view are formulated so easily and in such a variety of directions that they can afford much fruitful stimulus to physiological inquiry.

As the amino-acids are formed from the proteins, not only when these are subjected to the action of hot acids and alkalis but also at moderate temperatures by the agency of the digestive enzymes, they are to be regarded as the true foundation stones of protein molecules. Opinions adverse to this hypothesis are only occasionally met with; they centre round the arbitrary supposition that complicated atomic re-arrangements may take place during hydrolysis.

Were one inclined to regard such objections as of moment, all the experiments on the determination of the constitution of organic compounds by degradation methods would be useless; moreover, the conclusions which have been drawn in other cases from the results obtained by the dissection of compounds have been too frequently confirmed by their synthesis. It is now possible to make this claim on behalf of the proteins, as it has been found to be possible, by a process the reverse of hydrolysis, to associate amino-acids in such a manner that substances are produced which, in the case of the simpler terms, closely resemble peptones, whilst the more complex resemble proteins.

I have termed these synthetic products *polypeptides*, in view of their relationship to the peptones and to facilitate systematic treatment of the group on the lines followed in the case of the carbohydrates.

No useful purpose will be served by my giving an account of the synthetical methods on the present occasion, especially as I had the honour, six months ago, of describing to you the preparation of an octadecapeptide derived from fifteen molecules of glycine and three molecules of *l*-leucine, a substance which in its external properties closely resembles many natural proteins. I may say that more than one hundred of these artificial polypeptides have already been synthesised.

Many of them, it is true, belong to the lower stages but all the amino-acids previously mentioned, with the exception of diaminotrihydroxydodecanoic acid, have been made use of in their preparation. The synthesis of the higher terms has been restricted hitherto to the combinations of glycine, alanine and leucine; there is not a shadow of doubt, however, that all the remaining amino-acids could be associated in complicated systems with the aid of our present methods. The knowledge of the artificial polypeptides thus acquired has opened up new ways of investigating the peptones and albumoses analytically. During more than fifty years, physiological chemists have endeavoured without much success to isolate homogeneous substances from these ill-defined materials; all the products described by them, however, bear indubitable evidence of being mixtures. By making use of new methods based on the study of the polypeptides, it has been possible during the last two years to isolate and detect with certainty quite a number of dipeptides among the decomposition products of the proteins. In conjunction with Abderhalden, I have succeeded in separating glycyl-*d*-alanine, *d*-alanyl-*l*-leucine and *l*-leucyl-*d*-glutamic acid from silk fibroin, elastin and gliadin respectively. We have definitely proved the existence of dipeptides of glycine with *l*-leucine and *l*-tyrosine in the form of anhydrides and our work has made it probable that other combinations exist, for example, that of glycine with valine. P. A. Levene has discovered glycyl-proline anhydride among the products of the digestion of gelatine, whilst T. B. Osborne and S. H. Clapp have noted a dipeptide derived from phenylalanine and proline among the products of the hydrolysis of gliadin by hot sulphuric acid. A tetrapeptide of fairly definite composition has been isolated by Abderhalden and myself from silk fibroin; although its homogeneity is not yet quite established, it is certainly in great part a combination derived from two glycine molecules, one of *d*-alanine and one of *l*-tyrosine. The substance is of special interest on account of its close resemblance to the albumoses. Moreover, *l*-leucyl-triglycyl-*l*-tyrosine prepared artificially has all the properties of the albumoses. These observations are of importance as casting doubt on the view which formerly prevailed that, being intermediate products between proteins and peptones, the albumoses are substances of considerable molecular complexity. This may be true of many of the substances hitherto described under the name, all of which are certainly mixtures; but it is clear that many others are no more complex than the albumose above referred to from silk or the artificial pentapeptide.

In spite of these encouraging successes, I am fully aware of the difficulty of discovering the nature of all the components of the various peptones and albumoses. But in preparing the way for the synthesis of the natural proteins this is not even necessary. Probably the work can be restricted to the reconstruction of the original system from the major products of cleavage formed in the process of hydrolytic dissection. I am indeed venturesome enough to cherish the hope that I may be able to solve this problem in the case of silk fibroin, one of the simplest proteins. To deal with the whole of the proteins will be a gigantic task; so large a number of separate investigations will be necessary that nothing less than the life-work of a whole army of inventive and diligent chemists will suffice to complete it. Probably, too, the unpleasant discovery will be made that the natural proteins as we know them to-day are only to be obtained by mixing the homogeneous artificial products.

I have sketched this prospect merely to indicate the manner in which synthesis must play the leading part in this field of work. The nature of the more complicated carbohydrates, as I have already pointed out, will also have to be determined in the future, I imagine, mainly by the application of synthetic methods. Obviously the conditions are very similar in the case of the dextrins and gums to those met with in the case of the proteins; starch, which has hitherto been regarded as a homogeneous substance, appears also to come into the same category, according to Maquenne's observations.

Not only do the proteins constitute the major part of living protoplasm but they appear also to be the material from which the organism prepares its most wonderful agents: the ferments or enzymes. In many of the more thoroughly investigated biological processes their co-operation has been demonstrated and there is good reason to suppose that they take part in all changes occurring within the living cell. So much is certain, the physiological chemistry of the future will be largely concerned with the study of fermentative changes; many indications that this must be the case are to be met with in tracing its latest developments.

The number of the enzymes has been increased to an extraordinary extent during the last ten years. I may allude to the newly-discovered enzymes correlated with the carbohydrates: maltase, lactase, melibiase, trehalase, amygdalase, inulase; to the various oxidases: laccase, tyrosinase; to the lipases, erepsin, enterokinase, arginase, the sucroclastic and glucosidoclastic enzymes and finally to the zymase of alcoholic fermentation. Much valuable information has been accumulated as to the manner in which they act, as to their formation from zymogens and as to their assistance by co-ferments and their retardation by chemical agents or by antiferments. The specific character of their action, in other words, their dependence on the structure and configuration of the object they attack, has been proved beyond doubt and favours very definitely the assumption that enzyme and hydrolyte enter temporarily into combination, a conclusion to which H. E. Armstrong and E. F. Armstrong have quite recently again very properly drawn special attention. But, unfortunately, we know practically nothing of the composition of the enzymes, as the complete isolation of an enzyme has never been accomplished.

From observations hitherto made, it appears in a measure probable that they are derived from proteins and possess a protein-like character. If this be so, it may be hoped that the experience gained with the proteins will be of service in the investigation of enzymes.

In the meantime there are other directions in which synthetic chemistry can be of service in elucidating the chemistry of fermentation. In the same way that the artificial glucosides have been of use in establishing the dependence of the action of enzymes on configuration, the synthesised polypeptides are now being used by Abderhalden, Euler and others to define and measure the activity of the proteoclasts. In a like manner, the synthetic exploration of the purine group has served to direct the recent observations on the fermentative de-amination and oxidation of adenine, guanine and xanthine. Finally, attention may be directed to the use that has been made of stereochemical considerations in the course of Bertrand's interesting studies of the oxidation of polyhydric alcohols by the sorbose bacterium.

Not only have the methods of organic chemistry proved to be fruitful of results in the case of the proteins but also when applied to complex derivatives of the latter, such as the nucleo-proteins, for example. Thus we are indebted to the brilliant researches of A. Kossel and his school for our knowledge of no less than four bases of the pyrimidine and purine group obtained by breaking down nucleic acids; the analytical investigation of these latter has already been carried so far that, in the opinion of H. Steudel, it is to be expected that their synthesis will be effected at no distant date. Similar success may be hoped for even sooner in the case of the lecithins. Structural chemistry, moreover, is slowly acquiring the mastery over cholesterin by making use of the experience afforded by the synthetic study of the hydroaromatic substances.

Besides the old well known constituents of the animal body, new substances having quite unexpected properties have been added from time to time. Such are iodothyrin from the thyroid gland—discovered by Baumann—and crystalline adrenaline—isolated by Takamine from the supra-renal capsule—minute doses of which increase the blood-pressure. Judging from analytical results and the synthesis effected by F. Stolz, adrenaline possesses a relatively simple structure. In the opinion of the discoverers, this is probably true of the "pancreatic secretin" made known by Bayliss and Starling's researches, which has the remarkable property of liberating enzymes from the pancreas. May it not also be true of the toxins of many infectious diseases and of the antitoxins used in serum therapeutics, the discovery and systematic investigation of which by Behring, Roux, P. Ehrlich and others are to be reckoned among the greatest achievements of modern biology and medicine?

The methods of organic synthesis will certainly serve to throw light on the nature of all such substances of animal origin. The problems awaiting solution in the plant world are equally numerous.

The great success with which the alkaloids and terpenes have been studied during the past ten years is known to all but it is only too obvious that much still remains to be done when such substances as quinine, morphine and caoutchouc remain to be synthesised.

Alizarin and indigo are prepared artificially in huge quantities and we are well informed as to the structure of hæmatoxylin and kindred substances; but our ignorance is correspondingly great of most of the blood colouring matters as well as of many coloured constituents of our own bodies: of the hair, the skin and the eye.

The fullest recognition must be accorded, however, to recent investigations on the complex colouring matters of the blood and of chlorophyll, which is distantly related to the former, associated with the names of Schunck, Nencki, Marchlewski, Küster and Willstätter.

In fine, the aid of synthetical chemistry is required in every direction in arriving at a clear understanding of structure and of change. The methods at our disposal in the laboratory are doubtless altogether different from those which come into operation in the living world but chemists are already trying to effect changes in carbon compounds by means of so-called mild interactions, under conditions comparable with those which prevail in the living organism. It may suffice to refer to the development of a number of catalytic processes and to the comprehensive studies on the action of light on organic substances undertaken by Ciamician. In fact, the effort is already being made to co-operate with biology; it is clear that a section of the forces of organic chemistry is being directed once more towards the goal from which it set out. The separation from biology was necessary during the past century while experimental methods and theories were being elaborated; now that our science is provided with a powerful armoury of analytical and synthetical weapons, chemists can once more renew the alliance both to its own honour and to the advantage of biology. Indeed, the prospect of obtaining a clearer insight into the wondrous series of processes which constitute animal and vegetable life may well lead the two sciences to work with definite purpose to a common end.

In order, as far as possible, to avoid mistakes in this difficult task and to shield ourselves from the disappointment which is the inevitable consequence of exaggerated hopes, we cannot do better than strive to imitate the great example of Faraday, who always, with rare acumen, directed his attention to actual phenomena without allowing himself to be influenced by preconceived opinion, and who in his theoretical conceptions gave expression only to observed facts.

CLXV.—*The Occurrence of Quercitol (Quercite) in the Leaves of Chamaerops humilis.*

By Hugo Müller.

When collecting the materials for an article on Cellulose, which formed part of A. W. Hofmann's Report on the Chemistry at the Vienna Exhibition,* and treated of the application of cellulose in the arts, I had occasion to devise a method for estimating the amount of available fibre contained in the various new paper materials then proposed or in actual use.

Amongst the materials investigated were the leaves of *Chamaerops humilis*, the only European representative of the palm family, which at that time was imported from the Spanish province of Huelva to this country in some quantity and was used like esparto for making paper. During my examination of these leaves, I noticed that the aqueous extract, on becoming concentrated, deposited under favourable conditions a crystalline substance. This, on further investigation, proved to be quercitol, and I had subsequently an opportunity of preparing some quantity of it. The identity with quercitol from acorns was ascertained by its combustion, its chemical character, and melting point (230°), and the crystallographical measurement made at the time by Prof. N. Story Maskelyne afforded further confirmation.

Quercitol had previously only been found in the acorn, and in a minute quantity in cork and the bark of the oak; its occurrence in the leaves of a distinct family of plants is therefore of some interest, as we may hence expect it to be found more generally in the vegetable kingdom.

The quantity of quercitol yielded by the dry leaves of *Chamaerops* amounted to 1·35 per cent., and, considering the simplicity of the process by which it can be obtained from them, these leaves may prove a more suitable source than the acorns. For the purpose of preparing the quercitol, the crushed leaves are extracted with boiling water and the resulting liquid is precipitated first with neutral and then with basic lead acetate. After removing any lead in the filtrate, this is evaporated, when at the proper concentration the crystals of quercitol make their appearance.

With a special object in view, I recently repeated this operation with some fresh leaves of *Chamaerops humilis* kindly furnished by the Director of the Royal Gardens, Kew, and, in this case, a considerable quantity of the chlorides of potassium and sodium separated along with the quercitol. I am indebted to Prof. W. H. Perkin for kindly having this quercitol from *Chamaerops humilis* grown at Kew analysed at the Schunck Laboratory, Manchester University, with the following result:

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* *Bericht über die Entwicklung der Chemischen Industrie*, 1877.

0·1410 gave 0·2268 CO_2 and 0·0935 H_2O. C = 43·9; H = 7·3.

$C_6H_{12}O_5$ requires C = 43·9; H = 7·3 per cent.

In 1904, Messrs. Power and Tutin (Trans., 85, 624) discovered in the leaves of *Gymnema sylvestre* (Br.) (*Asclepiadaceae*) a new substance which had the composition, general properties, and constitution of quercitol, but proved to be its lævorotatory modification. It was therefore considered desirable to ascertain the specific rotation of the *Chamaerops*-quercitol, and Mr. Tutin, who kindly undertook to do this, found it to be $[\alpha]_D$ +23·9°, which is that of *d*-quercitol of the acorn.

CLXVI.—*Cocositol* (*Cocosite*), *a Constituent of the Leaves of* "*Cocos nucifera*" *and* "*Cocos plumosa.*"

By Hugo Müller.

The occurrence of quercitol in the leaves of a palm was deemed of sufficient interest for it to be sought for in the leaves of other species of this family. The then (1875) Director of the Royal Gardens, Kew, now Sir William Thiselton-Dyer, kindly gave me an opportunity of examining some of them and, in the first instance, supplied me with leaves of *Cocos plumosa* which could be conveniently spared at the time.

The green leaves were worked up in the manner indicated in the preceding paper on quercitol, but the result was negative, for not a trace of quercitol could be found. However, in the course of this examination, the somewhat considerable basic-lead-acetate precipitate had been saved and was decomposed in the usual manner with sulphuric acid.

The resulting liquid, after concentration to a thin syrup, had been left standing some time when some well-defined crystals made their appearance. These proved to be a new substance, resembling inosite in its chemical character and having the same composition, but differing widely in its physical properties.

This substance, which I propose for the present to name *cocosite*, was of sufficient interest to invite further investigation.

The Occurrence of Cocosite in Cocos Leaves from Various Sources.

Leaves of *Cocos plumosa* not being procurable, it was considered desirable to examine those of *Cocos nucifera* (the cocoa-nut palm) as being more accessible, and a preliminary trial with such leaves, also obtained from Kew, having proved the presence of cocosite, a quantity of the dry leaves of this palm were procured from Jamaica.

Unfortunately, the yield was but small, and the investigation had subsequently to be suspended for want of material and from other causes.

Recently, however, I have again taken up this work, and in the present communication I offer an account of the results thus far obtained.

For the continuation of this research, it was, in the first instance, necessary to secure a further supply of cocosite, and I availed myself of an opportunity of importing the cocos leaves from Barbados, for which I am indebted to Mr. J. R. Bovell, Superintendent of the Agricultural Department at Bridgetown. The quantity of cocosite derived from about 50 kilos. of these leaves was, however, very small, and the percentage so much less than that I had formerly obtained from the Jamaica leaves that I concluded this depended probably on the particular period of vegetation in which the leaves had been gathered. In order to ascertain this, I made arrangements during the last two years for receiving leaves at certain periods of growth and also from bearing and non-bearing trees. As even under the most favourable conditions the yield is but small, bulk samples of not less than 10 kilos. of the dry leaves were worked upon in each instance, and this entailed a great deal of protracted and tedious work. Without entering into further details, I may state here at once that no decisive results were, however, obtained.

Some of the samples yielded no cocosite, whilst others gave only traces, and at the best furnished very small quantities indeed of the desired substance.

In all these cases, the first part of the operation, namely, the extraction of the crushed leaves with water, was carried out for me in a factory, and, remembering the special conditions under which sorbinose is formed from the sap of the mountain-ash berries, it appeared worth while to see whether the presence of cocosite did not perhaps depend on some fermentative change accidentally induced in the previous operations of 1878, but such change being precluded in the recent experiments this might account for the variable and unsatisfactory results here recorded. With this view, the decoction of a sample lot was exposed to the air in a flat dish and allowed to become thoroughly mouldy before being worked up, but the result was entirely negative.

On the other hand, I repeated the original experiment with some quite fresh leaves of *Cocos plumosa*, which again were kindly supplied by the Director of Kew Gardens, and these yielded as before the cocosite in a very satisfactory manner and quantity, thus proving that it is contained ready formed in the growing leaf.

The cocos leaves received from Barbados having failed to furnish any adequate amount of cocosite, I had recourse to other sources, and I accepted the kind offer of Colonel Prain, the present Director of Kew Gardens, to procure for me a supply of leaves from the Royal Botanic Garden at Sibpur, Calcutta. I am indebted to Captain Gage, the Director, for a consignment of samples of leaves gathered in June, 1906, which I have lately finished working up.

These samples of leaves were designated as follows.

The leaves marked *A* are from the top of a tree cut down, of which the heart is sent as well as some of the outer leaves. Those marked 1, 2, and 3 respectively are from three different trees, three leaves from each, namely, a fully ripe leaf and a young leaf just expanded.

Those marked 1 are from a tree that is in flower, but has no fruit on it (this particular tree is the variety called by the Bengalees "Shwet Nargal," meaning white cocoa-nut); *№* 2 are leaves from a tree that is neither in flower nor in fruit, and *№* 3 are leaves from a tree that is in both flower and fruit.

Meanwhile I had also made arrangements for again obtaining a supply of leaves from Jamaica, as these had given such much more satisfactory results in 1878, and through the kindness of Mr. W. Fawcett, the Director of the Public Gardens and Plantation at Kingston, I obtained a few months ago a quantity which is now being worked up. The following table shows the great variability in the amount of cocosite obtained from the various kinds of leaves which were worked upon in quantity or examined as samples.

The Barbados leaves, having yielded such altogether insignificant quantities, are not taken into consideration.

	Leaves	of	*Cocos*	*plumosa*	from Kew……		0·23	per cent.
	,,	,,	*Cocos*	*nucifera*,	Jamaica,	1878	0·17	,, ,,
	,,	,,	,,	,,	,,	1907	0·05	,, ,,
№ 1	,,	,,	,,	,,	Sibpur, Calcutta		0·03	,, ,,
№ 2	,,	,,	,,	,,	,,	,,	0·03	,, ,,
№ 3	,,	,,	,,	,,	,,	,,	0·04	,, ,,
A	,,	,,	,,	,,	,,	,,	traces	

From this, it will be seen that the leaves of *Cocos plumosa* are the richest, and next to them come the cocoa-nut palm leaves from Jamaica obtained in 1878, but those imported from that island this year yielded only about one-third of the former.

On the other hand, out of the four samples from Calcutta, three contain about the same quantity, whilst the sample *A* gave only traces.* Quite recently, I have also completed some experiments with *Cocos nucifera* leaves from bearing and non-bearing trees, received from the Seychelles, but from neither of these have I obtained any cocosite.

Otherwise, all these trials give no clue whatever as to the supposed dependence of the amount of cocosite in the leaves on the particular vegetative condition or the season in which the leaves are gathered.

In the course of this work, the problem suggested itself that the cocosite might be contained also in the cocoanut, and, as these are readily obtainable, several trials were made. The so-called milk and the perisperm were examined. From 1 litre of the clear liquid obtained from fresh nuts a few centigrams of well-defined characteristic crystals of cocosite were obtained, but in 5 kilos. of the perisperm, which was worked up for this purpose, no cocosite was found.

Preparation of Cocosite from the Leaves.

For the purpose of extracting the cocosite from the leaves, I followed, in the main, until quite recently, the process indicated in the preceding paper on quercitol, and which is the mode of proceeding generally adopted in the investigation of the aqueous extract of plants. As the palm leaves are very stiff and hard, they are first reduced by means of a chaff-cutter and crushed, and then extracted by successive boilings with water. The clear, brownish-yellow liquid thus obtained is then first precipitated with neutral lead acetate and, after filtration, completely precipitated with a solution of basic lead acetate, of which a very considerable quantity is required on account of a very large amount of sodium and potassium chloride contained in the leaves.

This latter, very bulky, yellow precipitate thus obtained is well washed with distilled water and decomposed with sulphuric acid. The filtrate from the lead sulphate is then evaporated on a water- or steam-bath to a thick syrup or nearly to dryness, during which process much hydrochloric acid is given off and the liquid becomes very discoloured. On now redissolving this extract in cold water, a very considerable part, consisting of a dark brown, resinous substance mixed with silica, remains behind, and this occurs after repeating the evaporation and solution several times, hydrochloric acid being given off to the last.

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* The extracts of the Silpur leaves had been evaporated down to the consistency of a thick treacle, and, after some months' standing, in those of 1, 2, and 3 some rough crystals were noticed which proved to be cocosite. The extract *A* contained a larger amount of crystals, but they were found to be only the chlorides of potassium and sodium.

This operation is necessary in order to free the liquid as much as possible from a semi-gummy and a resinous matter which much impede the separation of the cocosite.

In more recent operations, I have treated the basic precipitate with a sufficient quantity of dilute acetic acid to produce an acid liquid, by which means the greater part of the chlorine and silica is retained in the precipitate, whilst the cocosite is now left in the liquid, from which any lead can be easily removed by the usual means.

Although not very readily soluble in water, the cocosite separates but slowly from the concentrated liquor, which requires to stand for some time unless the cocosite is present in some quantity. The separation of the cocosite can, however, be accelerated by the addition of alcohol to the liquid whilst hot, when, on cooling, the cocosite generally makes its appearance in more or less well-formed crystals. These, after recrystallisation and treatment with animal charcoal, are easily obtained in a pure state.

In the course of the further study of the chemical properties of cocosite, I was led to the working out of a modification of the above process, by which the troublesome precipitation with the lead acetate is superseded. I found that by the addition of milk of lime to the hot decoction of the leaves a very large amount of a gum, or pectine-like substance and colouring matter, is thrown down, amounting, in some of the trials, to as much as 50 per cent. of the solid matter contained in the extract. After removing this by filtration, the liquid is concentrated by evaporation on a water-bath. A hot concentrated solution of baryta is now added and the boiling continued for some time.

The baryta at first produces a dark yellow precipitate, which on further addition is followed by a heavier and paler precipitate. It may here be mentioned that the cocosite is mainly contained in the latter part of the precipitation. The baryta precipitate is filtered off whilst still hot and washed with hot water, then mixed with sufficient water, and carbon dioxide is passed into it until this is no longer absorbed. The liquid is now filtered off and concentrated by boiling, which causes the precipitation of the dissolved barium carbonate. When the proper concentration is reached, the cocosite separates in fine crystals, which are thus obtained colourless without the aid of animal charcoal, and after recrystallisation are chemically pure.*

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* In order to test the efficacy of this method, a quantitative experiment was made by adding one gram of cocosite to a quantity, usually operated upon, of leaf extract, which did not contain any cocosite, with the result that 0·92 gram of the cocosite was recovered.

Cocosite crystallises from water in beautiful, transparent and lustrous crystals, which, under favourable conditions, may be obtained 1 centimetre in diameter. It is not very soluble in cold water, and it was found that 100 c.c. of water at 15° dissolve 1·7 grams of cocosite, and 100 c.c. of water at 100° dissolve 8·3 grams.

It is insoluble in methyl or ethyl alcohol, ether, benzene, chloroform, or any other of the usual solvents.

When heated on platinum foil, the crystals first decrepitate, then melt, and take fire, burning with flame, like sugar, and leaving charcoal. When carefully melted and not over-heated in a glass tube, it forms a mobile, brown liquid, which, on cooling, suddenly solidifies and then bursts up into crystalline fragments.

The melting point was found to be at 345—350°, but this being so close to the limits of the mercury thermometer, the determination will have to be repeated on a future occasion with other and more reliable means.*

A saturated aqueous solution when tested exhibited no indication of optical activity.

On evaporating a hot solution, or on cooling a hot saturated solution, the cocosite separates in the characteristic form of short and stout crystals, which do not show any change when kept in the air even at an elevated temperature; but, on the other hand, if a cold, nearly saturated solution is gradually evaporated in a desiccator, crystals of a different habit appear; they are massive and long, prismatic, and after being removed and dried soon become opaque, white, and friable in consequence of the transformation into an aggregate of minute crystals. This change also takes place when these crystals are introduced into hot water. I have not been able to satisfy myself as to whether this change is due to a loss of water of crystallisation or to a change of crystalline form.

I am indebted to Mr. T. V. Barker, B.A., B.Sc. (Oxon.), of the Mineralogical Dept., University Museum, Oxford, who has kindly undertaken the crystallographical examination of this and the other crystalline compounds which are described in this communication.

Cocosite.

System: monoclinic.

Ratios of the axes: $a:b:c = 1{\cdot}7942:1:0{\cdot}7656$; $\beta = 117°12'$.

Forms: $m = \{110\}$, $c = \{001\}$, $o = \{111\}$, and $r = \{201\}$.

The habit of the crystals is shown in Fig. 1, the dominant forms being $m - \{010\}$, and $c - \{001\}$; r was rarely present. The faces afforded fairly good reflections, but rarely fell perfectly in zones.

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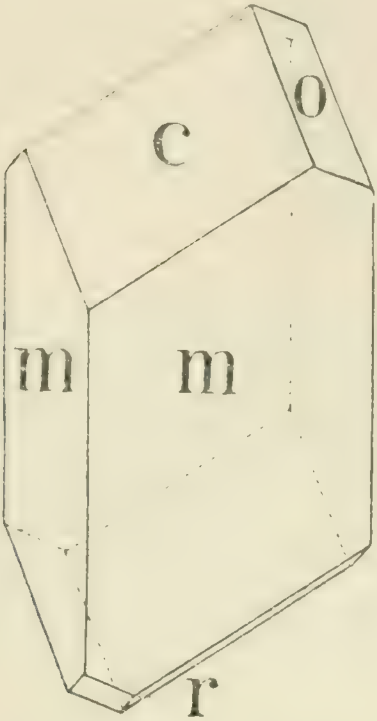
* Even mercury-thermometers filled with carbon dioxide and nitrogen seem soon to become untrustworthy after being used at these high temperatures.

The measurements were obtained from three selected crystals.

FIG. 1.



Angle.	No. of observations.	Limits.	Mean.	Calculated.	Diff.
$m : m = 110 : \bar{1}10$	8	63°58′—64°18′	64° 9′	—	—
$m : c = 1\bar{1}0 : 001$	9	75 53 —76 2	75 57	—	—
$c : o = 001 : 111$	9	43 35 —44 17	44 5	—	—
$o : m = \bar{1}11 : 110$	8	59 25 —60 29	59 56	59°58′	2′
$o : m = \bar{1}11 : 110$	4	57 53 —57 59	57 56	58 2	6
$o : r = \bar{1}11 : 201$	1	—	44 39	44 26	13
$r : m = 201 : 110$	1	—	77 32	77 32	0
$c : r = 001 : \dot{2}01$	1	—	51 22	51 13	9
$o : o = 111 : 111$	1	—	75 9	74 51	18

Cleavage: (001) good.

Optics: extinction on $m = 33°$ with edge mm. No characteristic interference figures are visible through c and m; birefringence, strong; one of the mean lines is almost perpendicular to $c - \{001\}$.

Specific gravity = 1·660; Mol. vol. = 108·5.

Topic axes: χ = 10·085, ψ = 5·6211; ω = 4·3035.

Two different preparations of cocosite were analysed:

I. 0·2215 gave 0·3220 CO_2 and 0·1357 H_2O. C = 39·74; H = 6·82.
II. 0·2092 ,, 0·3040 CO_2 ,, 0·1289 H_2O. C = 39·63; H = 6·84.
$C_6H_{12}O_6$ requires C = 40; H = 6·66 per cent.

A determination of the molecular weight by Beckmann's method was made with the following result.

To 15 c.c. of water boiling in the apparatus, 0·498 gram of cocosite was added as a first charge, when a rise of 0·090° took place, and on addition of the second charge of 0·497 gram a further rise of 0·10° was observed.

The latter, which is experimentally the more trustworthy result, gives 178·9 instead of 180 as required by the formula $C_6H_{12}O_6$.

Cocosite forms feeble, but defined, and, in some cases, well crystallised compounds, as, for instance, with potassium, sodium, and barium, and it is precipitated by basic lead acetate, which affords a means of separating and concentrating it in the process of its isolation from the aqueous extracts of plants.

When treated with acetic anhydride, it is converted into a *hexaacetate*; with benzoyl chloride it forms a *benzoate*; with nitric acid a corresponding *nitrate*, and with sulphuric acid several *sulphonic acids*.

Cocosite does not reduce Fehling's solution, but on boiling it with ammoniacal silver nitrate solution and an alkali a silver mirror is produced.

An aqueous bromine solution appears to have very little action on it, and even in sunlight the bromine disappears very slowly; but on the addition of a little iron in the form of bromide or other salt, a decided reaction takes place.

Cocosite gives the well-known and characteristic inosite reaction of Scherer; on heating it with nitric acid, evaporating carefully to dryness, redissolving the residue in water, adding a solution of calcium chloride, and again evaporating it, a fine red coloration is produced.

Cocosite and Potassium.

When to a hot solution of cocosite (1·5 grams in 30 c.c. of water) an alcoholic solution of potassium ethoxide is added, the mixture on cooling deposits brilliant crystals which, however, were found to contain not a trace of potassium. On redissolving the crystals and distilling off the alcohol, the same crystals of pure cocosite were again obtained on cooling. However, on dissolving the crystals once more and evaporating the liquid to about 100 c.c. and placing it in a desiccator over potassium hydroxide, a crop of beautiful, lustrous, short, prismatic crystals were obtained, which somewhat resembled cocosite, but, after being washed with alcohol, proved to be the desired *potassium* compound.

It seems to contain water of crystallisation, for the crystals, when dried at 100°, lose their lustre and become white. When heated on platinum foil, it melts and chars, producing at the same time a peculiar snake-like intumescence. On attempting to recrystallise it from water, it was decomposed, and again only pure cocosite crystallised from the solution.

Cocosite and Sodium.

This compound seems to be more stable, and is readily obtained on mixing a hot solution with a methyl-alcoholic solution of sodium hydroxide. On cooling, well-defined crystals formed, which were washed with alcohol and then kept for some time in a desiccator over potassium hydroxide.

1·6925 lost 0·127 H_2O at 100° ; $H_2O = 7·50$; on decomposing its solution with acetic acid and alcohol, 1·442 of cocosite was recovered, and the sodium acetate gave 0·582 Na_2SO_4. $Na = 11·1$.

$C_6H_{11}O_6Na,H_2O$ requires $H_2O = 8·2$; $Na = 10·5$ per cent.

Cocosite and Barium.

A solution of barium hydroxide causes no precipitate in a cold solution of cocosite ; but on heating the mixture and adding a hot concentrated solution of barium hydroxide, it becomes turbid, and a heavy, white, granular precipitate is formed, which increases on boiling if the solutions are of sufficient strength. This precipitate is more soluble in cold water than in hot, and on evaporating a solution the *barium* compound is obtained in small, but distinct, needle-shaped crystals.

Cocosite and Calcium.

On the addition of milk of lime to a solution of cocosite (1 in 200), a small quantity of the calcium hydroxide is at first dissolved ; but if an excess of it is added and the whole kept at the boiling point for some time, only a minute quantity of cocosite is found in the filtrate. The main part of it is retained in combination with the lime. This behaviour seemed to indicate a mode of preparing the cocosite from the leaf extract, but it was subsequently found that from the complex mixture of substances contained in the decoction of the leaves it is not the cocosite which is precipitated by the lime. Advantage is, however, taken of this in the mode of preparation of cocosite as previously described.

Cocosite Hexa-acetate.

Cocosite is but sparingly soluble in acetic anhydride, and may be boiled with it for some time without apparently being acted on, but on adding a small quantity of anhydrous sodium acetate, or, still better, fused zinc chloride, immediate reaction sets in.

Five grams of powdered cocosite, 50 c.c. of acetic anhydride, with 1·5 grams of zinc chloride, were boiled for several hours. The cocosite gradually dissolved, whilst glistening, small, prismatic crystals made their appearance, and towards the end of the operation caused the whole to become a semi-liquid magma.

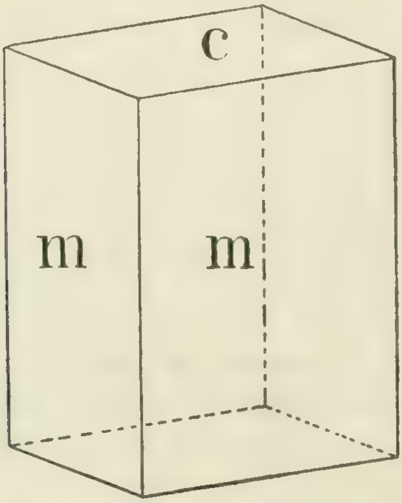
The product was boiled with water in order to hydrolyse the excess of acetic anhydride, then washed, and dried. It amounted in three different operations to 11·3, 11·8, and 11·9 grams. The last two results were obtained when the boiling was continued for five hours and zinc chloride was used. In the first operation, only 15 c.c. of acetic anhydride with five grams of sodium acetate was employed, and the boiling continued for only two hours.

Cocosite hexa-acetate is sparingly soluble in alcohol and most of the usual solvents, but from a hot solution in acetic anhydride it can be obtained in fine, prismatic crystals. It melts at about 300°, and in a tube at this temperature sublimes apparently without decomposition. On boiling it with a methyl-alcoholic solution of baryta, it is readily decomposed into cocosite and acetic acid. It was analysed with the following result:

0·2003 gave 0·3673 CO_2 and 0·1018 H_2O. C = 50·00; H = 5·65.

$C_6H_6(C_2H_3O)_6O_6$ requires C = 50·00; H = 5·55 per cent.

FIG. 2.



Cocosite Hexa-acetate.

The crystals were obtained from acetic anhydride.

System: monoclinic.

Ratios of the axes: $a:b:c = 0{\cdot}9222:1:\ ?$; $\beta = 97°33'$.

Forms: $m = \{110\}$, and $c = \{001\}$; the habit is shown in Fig. 2.

Angle.	No. of observations.	Limits.	Mean.	Calc.
$m:m = 110:1\bar{1}0$	12	84°49′—84°58′	84°52′	—
$c:m = 001:110$	13	84 13 —84 38	84 26	—

Cleavage: none observable.

Optics: extinction on m = 33 with the edge mm. An optic axis emerges obliquely through m; birefringence, medium.

Specific gravity: mean of three concordant determinations = 1·365.

Molecular vol.: 316·6.

Cocosite Benzoate.

On shaking for an hour 3 grams of cocosite dissolved in 150 c.c. of water with 18 c.c. of benzoyl chloride, which is gradually added alternately with a 20 per cent. sodium hydroxide solution, a white, crystalline substance, *cocosite benzoate*, formed, which weighed 1·7 grams.

In another experiment, 0·5 gram of finely-powdered cocosite was heated with 5 c.c. of benzoyl chloride to boiling. A white substance gradually began to be deposited on the walls of the tube, whilst hydrogen chloride was evolved. After heating for five hours, the semi-liquid contents of the tube were treated with a solution of sodium carbonate to decompose the excess of benzoyl chloride. The product of this operation amounted to 1·8 grams, which is a very much larger percentage than that of the former.

Cocosite benzoate melts at a temperature above the limit of the mercury thermometer, apparently without decomposition, and on cooling assumes a crystalline structure.

It is remarkable for its very slight solubility in all the usual solvents. Two analysis gave:

$C = 68{\cdot}82$ and $69{\cdot}06$; $H = 4{\cdot}62$ and $4{\cdot}55$.

$C_6H_7(C_7H_5O)_5O_6$ requires $C = 70{\cdot}28$; $H = 4{\cdot}58$ per cent.

Cocosite Nitrate.

Finely-powdered cocosite dissolves in concentrated nitric acid without any signs of decomposition. In order to prepare this compound, fuming nitric acid was employed, in which the powdered cocosite dissolved with great ease.

Four grams of cocosite were gradually introduced into about 10 c.c. of fuming nitric acid, and the mixture was then gently warmed to about 20°, when a clear solution was formed without any evolution of gas. To this solution, fuming sulphuric acid was gradually added, which caused a white, crystalline precipitate, accompanied by a considerable elevation of temperature, to appear. When 10 c.c. of the latter had been added, the whole became a white, semi-liquid magma. After standing until quite cold, the mass was gradually introduced into water and ice.

The nitrate thus formed was collected and thoroughly washed with water. The above quantity of 4 grams thus yielded 9·820 grams of the nitrate.

This substance is very insoluble in most of the ordinary solvents with the exception of boiling acetic anhydride, from which it crystallises on cooling in beautiful rhombohedra which probably belong to the rhombohedral system, since the angles between the several pairs of faces are the same, namely, 75°55′, the extinction in all the faces being diagonal. When heated in a test-tube, it explodes like guncotton without previous melting, filling the tube with nitrous fumes.

Two nitrogen determinations made of this substance gave $N = 14·22$ and 14·64, which would correspond to that of the *pentanitrate*, which requires $N = 14·4$ per cent., but these results require further confirmation.

A quantity of about 3 grams having been kept for several years was found to have undergone almost complete decomposition. Only a few decigrams of the original nitrate remained, and, besides some free nitric acid, oxalic acid, and some oxidation products which gave the rhodizonic acid reaction, the greater part of the residue consisted of cocosite which had been regenerated by spontaneous hydrolysis.

Cocosite Sulphonic Acids.

If crystals of cocosite are introduced into fuming sulphuric acid, no action appears to take place, but, on gently warming, the bright surface becomes white, owing to the formation of a sulphonic derivative. By raising the temperature, this is dissolved, and the crystals very gradually disappear.

To facilitate the reaction, the cocosite was finely powdered, and in one operation 3 grams were gradually introduced into 20 c.c. of fuming sulphuric acid. Very slight elevation of temperature took place, and, on applying heat, the thick mixture became liquid without discolouring. This liquid was poured on to a glass dish and left overnight. Lumps of ice were then added, and the liquid was gradually diluted with water without causing any perceptible elevation of temperature.

This liquid was then saturated with barium carbonate, filtered, and evaporated on the water-bath.

Two different *barium* salts were thus obtained in a crystalline form, the one much more insoluble than the other.

It was suspected that some of the more insoluble compounds adhered to the barium sulphate (although well washed with water), and on boiling this with dilute ammonium carbonate a small quantity of an *ammonium* salt was finally obtained on evaporation.

Action of Hydrogen Peroxide on Cocosite.

Hydrogen peroxide seems to have no action on a solution of cocosite at the ordinary temperature, but if, according to Fenton's method, a small amount of ferrous sulphate is introduced, the peroxide becomes active at once. The liquid at first turns yellow, and then on each further addition of small quantities of hydrogen peroxide a dark purplish-black coloration is produced, and the liquid becomes warm, without, however, any evolution of gas if the temperature is kept low by cooling. After a little while, the dark colour changes back into yellow, and finally a point is reached when further addition no longer produces any coloration. If the liquid is allowed to stand for a day or two, some greenish-yellow crystals of iron oxalate are deposited, and by means of a solution of calcium acetate free oxalic acid is removed. After filtration, the liquid is evaporated in a vacuum. On redissolving the dark-coloured product in water and adding barium hydroxide, a copious precipitate is formed which gradually turns red, and after any excess of baryta has been removed with acetic or dilute hydrochloric acid assumes a brilliant, red colour. This substance exhibits all the properties of a rhodizonate, and, like this, can be converted into a croconate. From these results, it would appear that the products of this reaction are similar to those obtained by the action of nitric acid on inosite, and that there are compounds formed which are probably nearly related to the tetrahydroxyquinone of Nietzki and Benckiser (*Ber.*, 1885, **18**, 499). Further investigation and experiments on a somewhat larger scale are, however, required to make this a certainty.

Action of Hydrobromic Acid on Cocosite.

For the further study of the chemical behaviour of cocosite, it was a matter of special interest to obtain some halogen derivatives. With this in view, some preliminary experiments were carried out by acting with a saturated solution of hydrogen bromide in glacial acetic acid on cocosite hexa-acetate after the manner described by Perkin and Simonsen (Trans., 1905, **87**, 855) and employed by them with so much success. The results thus obtained established a close analogy to those obtained with inosite hexa-acetate. These were carried out on a larger scale and are recorded in the paper on inosite (see below).

In 1887, C. Vincent and Delachanal (*Compt. rend.*, 1887, **104**, 1855) discovered and described a substance which they found in a very small quantity in some mother liquor of quercitol when preparing this from acorns, and which they named quercin. This substance has not again been noticed since that time, but it bears so strong a resemblance to cocosite that one would be tempted to pronounce them as identical were it not that, according to Aschan (*Ber.*, 1902, **35**, 3389), not less than nine stereoisomeric forms of hexahydroxy*cyclo*hexane, $C_6H_{12}O_6$, of which inosite is the representative, are possible. The probability of the identity of quercin and cocosite is strongly supported by the crystallographical data given for quercin by Friedel (*Compt. rend.*, 1887, **105**, 95) and these given by Mr. Barker for cocosite. There is also the scyllit, discovered by Staedeler and Frerichs (*J. pr. Chem.*, 1858, [i], **73**, 48), in the kidneys and other organs of certain plagiostomous fishes, which has quite recently been again prepared from the same source and more fully examined by Johannes Müller (*Ber.*, 1907, **40**, 1821). This also bears the closest resemblance to quercin and cocosite, but it must be left to further investigation to decide whether they are actually identical.

CLXVII.—*Inositol* (*Inosite*).

By Hugo Müller.

The difficulty which I experienced in securing a more abundant supply of cocosite (see preceding paper) for the continuation of its investigation led me to take up the study of the nearly related and isomeric inosite, of which I happened to possess a considerable quantity. This I had prepared years ago from the mother liquor of cochineal, in which I found it to be contained in appreciable quantity associated with tyrosine and guanine.

The behaviour of inosite would thus serve as a guide in the pursuit of the investigation of the cocosite, which would be all the more valuable as, on account of the great scarcity of this substance, the experiments with it have to be carried out with rather small quantities. In most cases, therefore, the experiments made with inosite preceded those made with cocosite.

The main object of the present communication is to give the results which have been obtained in the study of the reaction of a solution of hydrogen bromide in glacial acetic acid on inosite hexa-acetate.

As pointed out by Perkin and Simonsen (Trans., 1905, **87**, 855), this mode of bringing the hydrobromic acid into action affords a much more satisfactory and less destructive means than the employment of aqueous hydrobromic acid or the bromides of phosphorus.

I am indebted to Prof. W. H. Perkin, who had the compounds described in this paper analysed for me at the Schunck Laboratory, Manchester University, and also to Mr. T. V. Barker, who undertook their crystallographical investigation.

Inosite Hexa-acetate.

The inosite acetate used in this experiment was prepared by heating the anhydrous powdered inosite, in a flask provided with a long wide tube to act as a condenser, in quantities of 10 grams with 50 c.c. of acetic anhydride and 5 grams of fused zinc chloride. The reaction sets in with considerable energy, and continues without the further application of heat; but, in order to complete the operation, the contents of the flask were kept at the boiling point for about an hour, then allowed to cool, and the resulting scaly crystals repeatedly boiled with water. In this way, the theoretical quantity of hexa-acetate was invariably obtained.

The crystals were obtained from toluene.

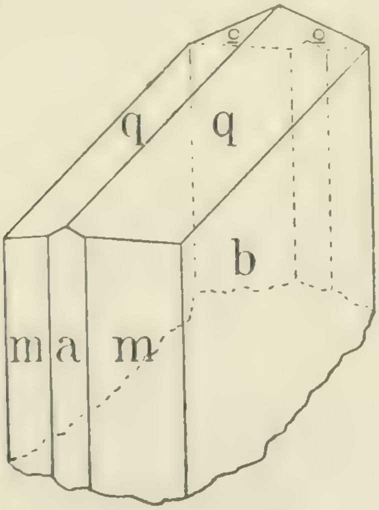
System: monoclinic.

Ratios of the axes: $a:b:c = 1{\cdot}1731:1:0{\cdot}4395$; $\beta = 101°58'$.

Forms: $b = \{010\}$, $q = \{011\}$, $m = \{110\}$, $a = \{100\}$, and $o = \{211\}$.

The habit is shown in Fig. 1. The form o was observed on one crystal only.

FIG. 1.



Angle.	Number of observations.	Limits.	Mean.	Calculated.
$b : q = 010 : 011$	11	66° 1′—68°40′	66°44′	—
$q : q' = 011 : 0\bar{1}1$	5	45 23 —47 30	46 23	46°32′
$b : m = 010 : 110$	8	39 6 — 43 20	41 4	—
$a : m = 100 : 110$	6	48 23 —50 51	48 59	48 56
$m : q = 110 : 011$	7	64 16 —65 27	64 59	—
$q : m' = 011 : \bar{1}10$	7	79 21 —80 49	79 58	80 3
$b : o = 010 : \bar{2}11$	1	—	67 41	67 56
$o : o' = \bar{2}11 : \bar{2}\bar{1}1$	1	—	circa 41°	42 4
$q : o = 011 : \bar{2}11$	1	—	,, 36	37 52
$o : a' = \bar{2}11 : \bar{1}00$	2	—	,, 62	63 6

Cleavage: none observable.

Optics: axial plane, normal to the symmetry plane; axial angle, wide; the first negative mean line makes an angle of 64° with the vertical axis in the acute angle β; birefringence, medium.

Specific gravity = 1·271. Mol. vol. = 340·04.

Topic axes: $\chi = 10{\cdot}286$, $\psi = 8{\cdot}7682$, $\omega = 3{\cdot}8539$.

This hexa-acetate, after recrystallisation from boiling alcohol, was now heated in quantities varying from 20 to 40 grams in sealed tubes with 50 c.c. or 100 c.c. respectively of glacial acetic acid saturated at 0° with hydrogen bromide, for eight hours at 100°, then for another eight hours at 150°, and finally allowed to cool.

No pressure was noticed on opening the tubes, and on emptying the contents into water, a thick, white, semi-liquid mass separated which gradually became nearly solid. On heating this with water, it formed a heavy, almost colourless liquid which on cooling again solidified. This mass was now treated with cold alcohol, which dissolved part of it, and left a white, chalky, indistinct, crystalline substance.

It was soon recognised that this was a mixture of several compounds, the complete separation of which proved subsequently to be beset with great difficulty, and became, in fact, a most tedious and laborious process.

The part dissolved in the alcohol consisted mainly of a viscid substance, insoluble in water, whilst another portion of the product retained in the aqueous acetic acid liquor was obtained in the form of an almost colourless, but amorphous, substance very soluble in water.

This multiplicity of substances formed in this reaction, although interesting, was somewhat embarrassing, and some special trials were consequently made with the view of ascertaining whether perhaps the degree of temperature, or time of reaction, had any influence in the formation of so many derivatives. These experiments, however, led to no tangible result and it became necessary subsequently to work up very considerable quantities of material in order to obtain the individual products in sufficient quantities for further examination.

In some of the operations, the contents of the tubes, after being mixed with water, were distilled in a vacuum in order to remove the acetic acid with the excess of hydrobromic acid, and it was then noticed that a small quantity of an oily liquid passed over with the first part of the distillate, which had the odour and other properties of bromobenzene.

For the further treatment of the white, chalky, crystalline product, recrystallisation from a suitable solvent was the only means of effecting the separation of its components, and after testing various solvents, such as alcohol, acetone, benzene, toluene, and glacial acetic acid, absolute alcohol proved in the end the most advantageous medium. Boiling alcohol dissolves the substance, but, on cooling, nearly the whole of it separates as a crystalline magma consisting of various kinds of crystals. If, however, a very large quantity of alcohol, about 50 parts, is used, small, white, indistinct crystals separate first, which are followed by scaly crystals, and then more massive crystals make their appearance, but there are no very marked intervals, and at first only partial separation is attainable by watching the progress of the crystallisation and removing immediately each kind of crystal by filtration through a suitably warmed filter before the separation of another form sets in. By repeating this process many times, the separation is finally effected.

The small, white, and indistinct crystals, which separate first as the less soluble, are *monobromoinosite penta-acetate,* the scaly and the massive crystals are two isomeric forms of *dibromoinosite tetra-acetate*; in addition, a fourth, more soluble substance, crystallising in needles, is contained in the alcoholic mother-liquor, but it has not yet been obtained sufficiently pure for analysis.

Monobromoinosite Penta-acetate.

This substance is deposited from its solution in the form of minute, indistinct, white crystals, which melt at 240°, and on cooling form a crystalline mass. It is insoluble in water; but soluble in benzene, toluene, chloroform, acetone, or glacial acetic acid, especially when warm. In cold alcohol it is very sparingly soluble, but more readily so on boiling. It was found that 0·5 gram required 75 c.c. of boiling absolute alcohol to dissolve it, whilst 100 c.c. of the saturated solution in the same medium at 20° only contained 0·015 gram. With a methyl-alcoholic solution of sodium methoxide, it becomes a deep orange-brown, and is decomposed by it on boiling. The solution thus formed reduces Fehling's solution. When heated with alcoholic ammonia in a sealed tube at 100°, it gradually dissolves and is decomposed. The colourless product is readily soluble in water, but has not yet been separated from the ammonium acetate and obtained in a crystalline condition.

When acted on by zinc, dust a reduction product is obtained (p. 1791). On analysis:

0·1852 gave 0·2873 CO_2 and 0·770 H_2O. C = 42·3; H = 4·6.
0·2843 „ 0·1209 AgBr. Br = 18·0.
$C_6H_6Br(O{\cdot}CO{\cdot}CH_3)_5$ requires C = 42·4; H = 4·6; Br = 17·7 per cent.

Dibromoinosite Tetra-acetate.

When quite pure, this substance can be obtained from its alcoholic solution in remarkably fine transparent crystals of more than a centimetre in diameter. It melts at 140° to a clear liquid, which on cooling forms a glass-like mass without any sign of crystallisation; but when scratched begins to crystallise and large, distinct crystals are formed in the solid mass.

It is insoluble in water, but soluble in glacial acetic acid, benzene, toluene, chloroform, or acetone, especially when hot. 100 c.c. of absolute alcohol at 20° dissolve 1·0 gram and 100 c.c. of boiling absolute alcohol dissolve 62·0 grams.

The hot alcoholic solution is a powerful solvent for the other compounds formed along with it by the action of hydrogen bromide on inosite hexa-acetate. When boiled with alcoholic potash, the alcoholic solution turns a deep orange-brown colour and reduces Fehling's solution. Alcoholic ammonia decomposes it gradually, even in the cold, without causing any coloration, and the presence of bromine is then indicated by the addition of silver nitrate.

When acted on by zinc dust, it is decomposed into acetic acid and phenol (p. 1790). On analysis:

0·2237 gave 0·2861 CO_2 and 0·0726 H_2O. C = 34·9; H = 3·7.
0·2207 „ 0·1740 AgBr. Br = 33·6.
$C_6H_6Br_2(O{\cdot}CO{\cdot}CH_3)_4$ requires C = 35·5; H = 3·8; Br = 33·7 per cent.

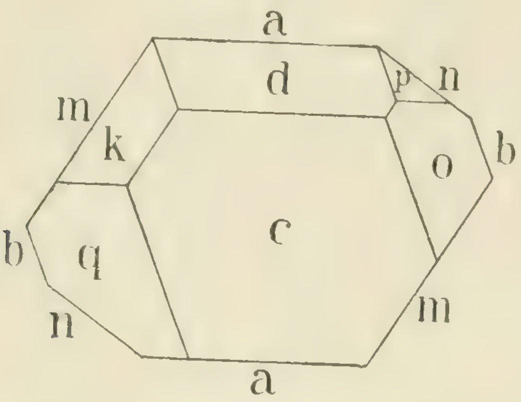
System: anorthic.

Ratios of the axes: $a:b:c = 1{\cdot}0644:1:0{\cdot}9153$, $\alpha = 112°10'$, $\beta = 116°7'$, $\gamma = 74°3'$.

Forms: $b = \{010\}$, $m = \{110\}$, $a = \{100\}$, $n = \{110\}$, $o = \{011\}$, $c = \{001\}$. $q = \{011\}$, $p = \{111\}$, $d = \{101\}$, $k = \{111\}$, $x = \{\bar{5}, \bar{7}, 12\}$, and $e = \{\bar{7}04\}$.

The habit of the crystals was slightly prismatic, the forms *m*, *a*, and *c* predominating. Of the remaining forms, *d*, *k*, *q*, and *n* were always of considerable size, whilst *o*, *p*, and *b* were more subordinate; *p* often failed, and *e* and *x* were observed but once (Fig. 2 is a projection normal to the prism zone).

FIG. 2.



Angle.	No. of observations.	Limits.	Mean.	Calc.	Diff.
$b : m = 010 : 110$	11	47°36′—48° 2′	47°49′	47°44′	5′
$m : a = 110 : 100$	20	49 33 —50 6	49 47	—	—
$a : n = 100 : 1\bar{1}0$	17	41 44 —42 17	42 2	—	—
$n : b' = 1\bar{1}0 : 0\bar{1}0$	12	40 2 —40 38	40 23	40 27	4
$b : o = 010 : 011$	12	39 33 —39 42	39 38	39 39	1
$o : c = 011 : 001$	18	33 0 —33 21	33 9	33 4	5
$c : q = 001 : 0\bar{1}1$	19	47 12 —47 40	47 23	47 31	11
$q : b' = 0\bar{1}1 : 0\bar{1}0$	15	59 39 —59 59	59 49	59 42	7
$b : c = 010 : 001$	3	72 37 —72 44	72 42	72 43	1
$b : p = 010 : \bar{1}11$	1	—	36 49	36 55	6
$p : d = \bar{1}11 : \bar{1}01$	3	29 48 —29 54	29 51	29 54	3
$d : k = \bar{1}01 : \bar{1}\bar{1}1$	13	48 15 —48 40	48 32	48 34	2
$k : b' = \bar{1}\bar{1}1 : 0\bar{1}0$	9	64 39 —64 46	64 44	64 37	7
$b : d = 010 : \bar{1}01$	6	66 37 —66 57	66 42	66 49	7
$m : o = 110 : 011$	12	43 25 —43 41	43 31	43 28	3
$o : d = 011 : \bar{1}01$	10	47 36 —47 49	47 43	47 52	9
$d : m' = \bar{1}01 : \bar{1}\bar{1}0$	9	88 40 —88 59	88 45	88 40	5
$m : c = 110 : 001$	24	59 11 —59 30	59 17	—	—
$c : k = 001 : \bar{1}\bar{1}1$	15	65 14 —65 51	65 28	65 34	6
$k : m' = \bar{1}\bar{1}1 : \bar{1}\bar{1}0$	15	54 53 —55 25	55 14	55 9	5
$m : q = 101 : 0\bar{1}1$	14	93 3 —93 19	93 11	93 20	9
$m : p = 110 : \bar{1}11$	4	69 33 —69 38	69 36	69 33	3
$a : o = 100 : 011$	7	79 37 —80 11	79 55	79 45	10
$o : p = 011 : \bar{1}11$	2	31 5 —31 8	31 6	31 9	3
$p : a' = \bar{1}11 : \bar{1}00$	2	68 51 —69 2	68 57	69 6	9
$o : a' = 011 : \bar{1}00$	5	99 56 —100 20	100 7	100 15	8

Angle.	No. of observations.	Limits.	Mean.	Calc.	Diff.
$a : c = 100 : 001$	24	67 39 – 67 56	67 48	—	—
$c : d = 001 : \bar{1}01$	16	47 53 —48 27	48 9	—	—
$d : a' = \bar{1}01 : \bar{1}00$	16	63 50 —64 19	64 2	64 3	1
$r : c = 001 : \bar{7}04$	1	—	72 58	72 23	35
$a : q = 100 : 0\bar{1}1$	13	63 25 —63 52	63 37	63 43	6
$q : k = 011 : \bar{1}\bar{1}1$	13	44 55 —45 21	45 7	45 8	1
$k : a' = \bar{1}\bar{1}1 : \bar{1}00$	10	71 1 —71 20	71 12	71 9	3
$n' : o = \bar{1}10 : 011$	17	66 2 —66 15	66 9	66 12	3
$n : c = 1\bar{1}0 : 001$	10	87 10 —87 24	87 16	87 19	3
$c : p = 001 : \bar{1}11$	1	—	53 30	53 21	9
$p : n' = \bar{1}11 : \bar{1}10$	1	—	39 7	39 20	13
$c : n' = 001 : \bar{1}10$	9	92 38 —92 53	92 44	92 41	3
$n : q = 1\bar{1}0 : 0\bar{1}1$	12	50 44 —51 6	50 55	50 55	0
$q : d = 0\bar{1}1 : \bar{1}01$	10	72 23 —72 44	72 38	72 36	2
$d : n' = \bar{1}01 : \bar{1}10$	10	56 18 —56 29	56 23	56 29	6
$q : x = 011 : \bar{5} : \bar{7} \cdot 12$	1	—	27 37	27 53	16
$n : k = 1\bar{1}0 : \bar{1}\bar{1}1$	10	85 29 —85 37	85 35	85 31	4
$p : k = 011 : \bar{1}\bar{1}1$	10	87 57 —88 10	88 1	88 11	10
$q : p = 0\bar{1}1 : \bar{1}11$	2	94 17 —94 18	94 17	94 28	11

Cleavage: perfect parallel to *a* – (100).

Optics: extinction on *a* makes an angle of 4° with the edge *a* : *m*; on *m*, an angle of 17° with the same edge; the extinction on *c* is 30° with the edge *ca*. An optic axis emerges obliquely through *d*. The birefringence is strong.

Specific gravity: two concordant determinations gave the mean value: Sp. gr. 18°/4° = 1·713. Mol. vol. = 276·74.

Topic axes: $\chi = 7{\cdot}4623$, $\psi = 7{\cdot}0108$, $\omega = 6{\cdot}4169$.

Dibromoinosite Tetra-acetate; Scaly Modification.

The main difference of this isomeric modification from that just described consists in its crystalline form and in the less degree of solubility in the various solvents. It invariably crystallises from its solvents in glistening, thin scales; but under favourable conditions may be obtained from a solution in toluene in more defined crystals.

It melts at 235° to a clear liquid, which on cooling becomes a foliated, crystalline solid.

100 c.c. of a saturated solution in absolute alcohol at 20° contain only 0·18 gram, whilst 100 c.c. of boiling absolute alcohol dissolve 3·6 grams.

Methyl-alcoholic soda, even in the cold, causes a deep orange-brown coloration, and readily decomposes it on boiling. The solution reduces Fehling's solution. On analysis:

0·2314 gave 0·3031 CO_2 and 0·0781 H_2O. C = 35·7; H = 3·8.
0·3371 „ 0·2655 AgBr; Br = 33·6.
$C_6H_6Br_2(O{\cdot}CO{\cdot}CH_3)_4$ requires C = 35·5; H = 3·8; Br = 33·7 per cent.

This modification generally crystallises in very small, slender scales, quite unsuited for crystallographic investigation, but a measurable crop was finally obtained by slowly cooling a toluene solution.

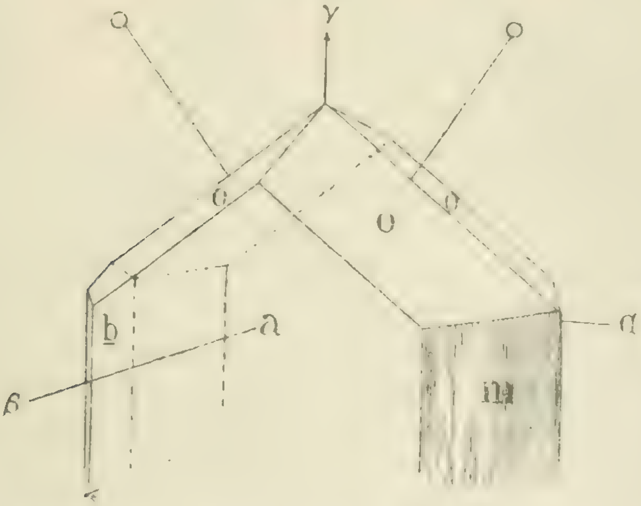
System: orthorhombic (holo-axial?).

Ratios of the axes: $a : b : c = 2·790 : 1 : 0·758$.

Forms: $a = \{100\}$, $o = \{111\}$, $m = \{110\}$, $b = \{0\bar{1}0\}$, and $n = \{430\}$.

The habit is shown in Fig. 3; the prism zone was characterised by a series of vicinal and curved faces, especially at the positive end of the axis *b*. The form *b* always consisted of a single face (010), and as the crystals were never doubly terminated they may therefore be holo-axial. The form *n* was only observed once.

FIG. 3.



Angle.	Number of observations.	Limits.	Mean.	Calculated.
$a : m = 100 : 110$	5	70°11′—70°31′	70°17′	—
$a : n = 100 : 430$	1	—	64 32	64°28′
$o : o = 111 : 1\bar{1}1$	6	71 56 —72 42	72 22	—
$o : o = 111 : \bar{1}11$	2	25 37 —26 8	25 52	24 26
$o : a = 111 : 100$	1	—	78 19	77 47
$o : o = 111 : \bar{1}\bar{1}1$	2	77 53 —78 18	78 5	77 41
$o : m = 111 : 110$	1	—	51 1	51 10

Cleavage: perfect parallel to *a*, fairly good parallel to *m*.

Optics: axial plane parallel to *a*; first positive mean line normal to *c* – (001); axial angle very wide; birefringence strong.

Sp. gr. 17°/4° = 1·693. Mol. vol. = 280·01.

Topic axes: $\chi = 14{\cdot}220$, $\psi = 5{\cdot}097$, $\omega = 3{\cdot}863$.

Up to the present, there is no indication of the formation of a higher brominated derivative than the dibromo-tetra-acetate when inosite hexa-acetate is treated with excess of hydrogen bromide at 150°.

Inosite Dibromohydrin.

In the course of the earlier experiments, when dealing with the viscid part extracted by cold alcohol from the original crude product, it was noticed that on boiling it for some time with water for the purpose of removing the last traces of hydrobromic and acetic acids it gradually dissolved. On evaporating the resulting liquid and allowing it to stand for some time, a crystalline substance separated from the syrupy mother liquor.

The same substance was also obtained when the aqueous washing liquor of the original product referred to above as containing an amorphous substance was repeatedly evaporated in a vacuum and re-dissolved to remove all hydrobromic and acetic acid, and the resulting thick liquid allowed to stand for some time.

The crystalline substance, after being freed as much as possible from the mother liquor by means of a suction filter and pressure between bibulous paper, was crystallised from water, and thus obtained in remarkably fine massive crystals which are quite colourless and of great brilliancy.

This substance is *inosite dibromohydrin*, and is evidently the product of hydrolysis of a dibromoinosite acetate. It melts at 210° with partial decomposition, becoming brown and giving off hydrogen bromide. It is readily soluble in water, less so in alcohol or glacial acetic acid, and insoluble in ether, benzene, or acetone.

100 c.c. of a saturated solution in water at 20° contain 3·15 grams, and 100 c.c. of a boiling aqueous solution contain 60·00 grams; 100 c.c. of a saturated solution in absolute alcohol at 20° contain 0·55 gram, whilst 100 c.c. of a boiling solution in absolute alcohol contain 6·00 grams.

Silver nitrate added to the aqueous solution gives after a while a slight turbidity, which increases on boiling. Caustic alkalis produce a dark brown coloration on boiling, and Fehling's solution is reduced by it. On analysis:

0·1876 gave 0·1634 CO_2 and 0·0577 H_2O. C = 23·7; H = 3·4.
0·2095 „ 0·1801 CO_2 „ 0·0570 H_2O. C = 23·4; H = 3·0.

0·1557 gave 0·1353 CO_2 and 0·0479 H_2O. C = 23·7 ; H = 3·4.
0·5275 „ 0·6471 AgBr. Br = 52·2.
0·3152 „ 0·3880 AgBr. Br = 52·4.
$C_6H_{10}O_4Br_2$ requires C = 23·5 ; H = 3·3 ; Br = 52·2 per cent.

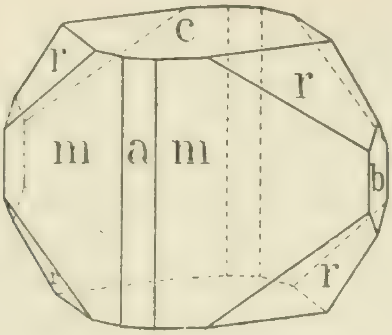
System : orthorhombic.

Ratios of the axes : $a : b : c = 0·7726 : 1 : 0·7654$.

Forms : $m = \{110\}$, $c = \{001\}$, $r = \{121\}$, $b = \{010\}$, and $a = \{100\}$.

The habit was generally tabular, parallel to the basal plane ; a few crystals, however, were considerably elongated along the vertical axis. A typical crystal is shown in Fig. 4.

FIG. 4.



Angle.	No. of observations.	Limits.	Mean.	Calc.	Diff.
$m : a = 110 : 100$	22	37°21′— 38° 0′	37°37′	37°41′	4′
$m : b = 110 : 010$	24	52 7 — 53 3	52 22	52 18	4
$r : c = 121 : 001$	10	61 11 — 61 21	61 15	61 16	1
$r : r = 121 : 121$	11	122 10 —122 53	122 32	122 31	1
$r : a = 121 : 100$	28	61 8 — 61 58	61 32	61 33	1
$r : r = 121 : \bar{1}21$	13	56 36 — 57 7	56 52	56 54	2
$r : b = 121 : 010$	17	42 21 — 42 52	42 37	42 36	1
$r : r = 121 : \bar{1}2\bar{1}$	5	84 56 — 85 31	85 15	85 12	3
$m : r = 110 : 121$	8	33 40 — 34 42	34 7	34 12	5
$[cr] : [cr']$	5	65 37 — 66 11	65 50	65 49	1

The fundamental angles used were : $r : a : 61°33'$, $r : c = 61°16'$, these being the means of all the angles in the two zones. The prism faces rarely fall in the zone ab, and seem to be always vicinal ; a good agreement between the observed and calculated angles is not obtained when the prism angles are used as fundamental angles.

No good cleavage was observed.

Optical properties: the crystals are biaxial, which proves that this substance, although pseudo-tetragonal, is really orthorhombic; the first mean line is normal to the pinacoid, $a-(100)$, and is positive. Plane of the optic axes $b-(010)$; birefringence, strong; dispersion, $\rho < v$.

Two plates were ground, perpendicular to the acute and obtuse bisectrices respectively, and the axial angle was calculated from observations of 2Ha and 2Ho in cedar oil, sodium light being used: $2E = 67°30'$.

Specific gravity, two determinations were made: mean, $D22°/4° = 2·337$. Mol. vol. $= 130·94$.

Topic axes: $\chi = 4·6741$, $\psi = 6·0495$, $\omega = 4·6307$.

It was found that the brominated inosite hexa-acetate is hydrolysed by boiling with hydrochloric or hydrobromic acid, and it therefore seems probable that during the action of hydrobromic acid on the hexa-acetate some of the brominated hexa-acetate formed is partly hydrolysed, and that, in fact, the viscid part (insoluble in water) of the product is a derivative intermediate between the dibromo-hexa-acetate and inosite dibromohydrin.

As, however, this viscid compound could not be obtained in a condition fit for analysis, this must for the present remain a surmise.

This also applies to the substance contained in the final aqueous mother liquor, which is obtained in the form of a colourless or slightly yellow substance, resembling gum arabic and containing bromine but in what relation it stands to the crystallised bromohydrin has still to be ascertained.

Products of Debromination by Means of Zinc Dust.

Having now obtained some of the bromo-derivatives in a definite form, their further examination could be proceeded with, and the study of their behaviour towards reducing agents naturally suggested itself. As a somewhat larger quantity of the dibromo-tetra-acetate, crystallising in massive crystals, was at disposal, this was taken in hand first.

In a small retort, connected with a condenser, 5 grams of the crystals were dissolved in 30 c.c. glacial acetic acid and to the cold solution 5 grams of zinc dust were gradually added. No hydrogen was given off, but a reaction was indicated by the agglomeration of the zinc dust particles, and the presence of bromine in the solution could soon be detected by silver nitrate. The reaction was finally assisted by the application of a minute gas flame, and the operation discontinued as soon as the addition of water to some of the liquid taken from the retort no longer caused a precipitate of the original substance. The contents of the retort were then mixed with much water, and the residue (mainly cadmium) of the zinc dust filtered off.

The filtrate was then precipitated with a hot solution of silver acetate, and the filtrate from the silver bromide treated with hydrogen sulphide to remove the zinc. On finally evaporating the liquid, there was nothing left except a trace of zinc bromide. The whole of the 5 grams of the substance acted on had thus disappeared.

During the evaporation of the liquid, there was besides that of acetic acid a distinct phenolic odour perceptible, and consequently on repeating the experiment with a fresh quantity of the substance the contents of the retort, after the treatment with zinc dust, were simply mixed with water and distilled. From the milky distillate whic passed over, a heavy oil separated which had the general properties of phenol, and tribromophenol and phenyl benzoate were obtained from it; it failed, however, to give satisfactory colour tests with ferric chloride and bleaching powder solution. Subsequently it became evident that this was caused by the presence of acetic acid. In this second experiment, the aqueous liquid remaining after distillation was again treated with silver acetate to remove the bromine, then with hydrogen sulphide to remove the zinc, and finally evaporated, when nothing was left.

On submitting the scaly form of the dibromo-tetra-acetate to the same treatment, the experiment was carried out at a somewhat higher temperature on account of the more sparing solubility of this substance, but the result was precisely the same as in the former case.

Phenol seems then to be the only product of this reaction, and no other substance could be detected which might indicate the intermediate stages of the process which obviously must intervene.

This reaction presents some features of considerable interest. As already mentioned, the dibromo-tetra-acetates on prolonged boiling with acids, such as hydrochloric or hydrobromic, are hydrolysed, but it was found that with glacial acetic acid no perceptible change is produced. The addition of zinc dust to the latter, however, even at a low temperature, not only induces the hydrolysis, but, in the act of eliminating the bromine, breaks down the inosite molecule to phenol.

It became now a matter of special interest to study the behaviour of the monobromo-penta-acetate under the same treatment, and for this purpose 5 grams of the substance with 30 c.c. of glacial acetic acid were introduced into a retort and 5 grams of zinc dust stirred into the mixture; but as the substance is only slightly soluble, the retort was gently warmed. Very little hydrogen was given off, and the substance gradually dissolved. After the lapse of six hours, the retort was allowed to cool, when it was noticed that the contents remained liquid, an indication that a reaction had taken place.

The addition of water now caused the separation of a colourless, crystalline substance which, on warming, melted and formed a heavy oil, which again became crystalline on cooling. After recrystallising it from dilute alcohol, it separated in soft, slender, prismatic crystals melting at 95°. This substance is readily soluble in alcohol, but less so in water. It was dried in an evacuated desiccator over sulphuric acid:

0·1214 gave 0·2380 CO_2 and 0·0663 H_2O. $C = 53·4$; $H = 6·0$.

Average of three analyses: $C = 53·3$; $H = 5·9$.

$C_{14}H_{18}O_8$ requires $C = 53·5$; $H = 5·7$ per cent.

Accordingly, we must assume that in this case the original substance, $C_{16}H_{21}O_{10}Br$, is reduced to $C_{16}H_{22}O_{10}$, and this then loses acetic acid.

To test this view, an exact determination of the acetyl groups is required, which, however, had to be postponed on account of want of material.

In the mother liquor of this substance, another compound was found, which separates from the aqueous solution on concentration as a colourless, heavy oil remaining liquid at the ordinary temperature for some time and then becoming a crystalline solid. This substance also awaits further examination.

Inosite and Hydrogen Peroxide.

The description given under the heading, "Action of Hydrogen Peroxide on Cocosite," in the preceding paper (p. 1779), applies in every detail to what takes place when inosite is submitted to the same treatment. The transient, deep purple-blue coloration makes its appearance in the same manner, and finally a stage is reached when further addition of hydrogen peroxide no longer produces this effect. No carbon dioxide is evolved if the addition of the dilute hydrogen peroxide is made in small quantities, and time allowed for the disappearance of the colour in the intervals. Some oxalic acid is formed, which was removed by adding a solution of calcium acetate, and after filtration the liquid was concentrated in a vacuum. By this time, it had become coloured, and in the course of a few days, after exposure to the air, had turned quite dark. On evaporating it further on the water-bath and allowing it to stand in a desiccator, it became dry, but no signs of crystallisation appeared. Its solution readily reduced Fehling's solution, and the characteristic barium rhodizonate was obtained from it; but up to the present I have not been able actually to identify the substance or substances contained in this oxidation product of inosite.

In conjunction with these experiments, trials with other oxidising agents, such as aqueous bromine in presence of iron and platinum black, are being made, which promise to yield results.

Also the action of an ammoniacal solution of silver carbonate has been investigated. A solution of 5 grams of inosite in dilute ammonia was heated to boiling in a retort, and moist silver carbonate added to it at intervals. The silver was thus freely reduced and crystals of ammonium carbonate appeared in the neck of the retort. When no further reduction of silver took place, the operation was discontinued, the liquid filtered off and evaporated. The silver residue, on the other hand, was extracted with dilute hydrochloric acid, and after filtration the acid liquid evaporated on a water-bath. The former yielded a small quantity of ammonium oxalate, whilst from the latter nothing but oxalic acid was obtained. As this result seemed to indicate that the reaction had been carried too far, the experiment was repeated with a less amount of silver carbonate. But in this case also, although some unchanged inosite was recovered, no other substance besides oxalic acid could be found.

In conclusion, I beg to offer my thanks to the managers of the Davy-Faraday Laboratory for having afforded me the opportunity of carrying out these investigations.

Davy-Faraday Laboratory,
Royal Institution.

CLXVIII.—*Hydrates of Some Quaternary Bases.*

By David Cowan Crichton (Carnegie Research Scholar).

Walker and Johnston (Trans., 1905, **87**, 955) have described a method for preparing tetramethylammonium hydroxide by the interaction of potassium hydroxide and tetramethylammonium chloride in alcoholic solution, and have shown how definite hydrates of the quaternary base may be separated from the solution obtained. At Prof. Walker's suggestion I have prepared by the same method solutions of tetraethylammonium and tetrapropylammonium hydroxides and of trimethylsulphine hydroxide, and in this paper hydrates of the first two bases are described.

Tetraethylammonium Hydroxide.

The preparation of this base was conducted as follows: 11·5 grams of potassium hydroxide, dissolved in eight times its weight of methyl alcohol, were mixed with 33·9 grams, the equivalent quantity, of tetraethylammonium chloride dissolved in its own weight of methyl alcohol. A bulky precipitate of potassium chloride at once separated and was removed after an hour's interval by filtration through an asbestos filter, the operation being carried out as rapidly as possible by the aid of the pump in an atmosphere free from carbon dioxide. The filtrate was transferred to a large distilling flask and to it were added 100 c.c. of water. The methyl alcohol and a portion of the water were then removed under diminished pressure at a temperature not exceeding 50°. When the distillation had continued for three hours, the liquid, which then contained 44 per cent. of anhydrous base, was placed in a vacuous desiccator charged with phosphorus pentoxide. In the course of a few days, the liquid partly set to a mass of fine needles, which were separated by filtration on an asbestos filter, and preserved in a closed glass-box in a desiccator. A second quantity of the hydrate was prepared in a similar way, 47·5 grams of crystalline base in all being obtained from 70 grams of the chloride.

The crystals were proved to be free from potassium and from chlorine, and titration showed them to contain four molecules of water of crystallisation.

I. 0·2442 required 44·1 c.c. of $N/40$ HCl. Equiv. = 221.
II. 0·1563 ,, 27·3 ,, ,, ,, 229.
III. 0·1050 ,, 19·4 ,, ,, ,, 221.

$N(C_2H_5)_4OH,4H_2O$ has the equivalent 219.

Analysis of the crystals dried in a vacuum resulted as follows:

I. 0·1472 gave 7·76 c.c. of nitrogen at N.T.P. N = 6·60.
II. 0·2014 ,, 10·84 ,, ,, N = 6·73.
III. 0·3957 ,, 0·5823 CO_2 and 0·4343 H_2O. C = 44·14; H = 13·41.
IV. 0·1612 ,, 0·2612 CO_2 ,, 0·1915 H_2O. C = 44·19; H = 13·20.
$N(C_2H_5)_4OH,4H_2O$ requires C = 43·84; H = 13·25; N = 6·39 per cent.

A *tetrahydrate* of tetraethylammonium hydroxide thus separates from aqueous solution instead of a pentahydrate as is the case with tetramethylammonium hydroxide under the same conditions.

Tubes containing small weighed quantities of the tetrahydrate were preserved over phosphorus pentoxide at various temperatures and pressures in order to ascertain if it were possible to dehydrate the hydrate wholly or partly. At the ordinary temperature and pressure, the loss of weight is very slow, but in an evacuated space decomposition proceeds with considerable rapidity. Thus 0·2276 gram at 25°

in a vacuous desiccator was found to have lost 0·046 gram in three days. The loss, however, was not due to dehydration alone, for the residual solid on titration was found to possess the equivalent 217, that is, practically the equivalent of the tetrahydrate. Another portion, weighing 0·1169 gram, lost 0·0224 gram in two days at 15° in a tube evacuated by means of a mercury pump. The residue on titration showed the equivalent weight of 220. It is apparent from these experiments that the tetrahydrate when it loses water also decomposes even at the ordinary temperature, as the hydroxide is not in itself volatile. As the decomposition observed by Hofmann at 100° was in the sense of the equation (*Annalen*, 1851, **78**, 268) :

$$N(C_2H_5)_4OH = N(C_2H_5)_3 + C_2H_4 + H_2O,$$

the gaseous contents of one of the tubes (originally evacuated by means of a Krafft mercury pump) were collected by the aid of a Sprengel pump, and were found on analysis to consist of practically pure ethylene. It is thus impossible directly to dehydrate the tetrahydrate of tetraethylammonium hydroxide at or above the ordinary temperature without the base itself undergoing decomposition. This behaviour is in sharp contrast to that of tetramethylammonium hydroxide, which can be dehydrated to the stage of monohydrate before decomposition sets in (Walker and Johnston, *loc. cit.*, p. 960).

The crystals of tetrahydrate are extremely soluble in water, dissolving with considerable absorption of heat. They melt at 49—50° without perceptible decomposition.

The comparative strength of the base as against sodium hydroxide was determined in $N/100$ solution by the rate of saponification of ethyl acetate, using Walker's conductivity method (*Proc. Roy. Soc.*, 1906, **78**, *A*, 152). It was found that if the strength of sodium hydroxide in centinormal solution is represented by 100, that of tetraethylammonium hydroxide in equivalent solution is represented by 95.

Hexahydrate.—The filtrate from the original preparation of tetrahydrate was found, when it had stood for some days in a desiccator, to have deposited a further quantity of crystals, larger in size than those of the original crop. These were dried on porous porcelain and titrated with the following result :

0·0933 required 14·35 c.c. $N/40$ HCl. Equiv. = 260.
0·1873 „ 29·4 „ „ 255.

$N(C_2H_5)_4OH,6H_2O$ has the equivalent 255.

The composition is that of a hexahydrate. When heated, the hexahydrate melts at 50°. A portion which had been melted and allowed to resolidify gave the following result on titration :

0·2217 required 35·0 c.c. $N/40$ HCl. Equiv. = 255.

The hexahydrate can thus be melted without fundamental change. At 55°, however, the liquid obtained by fusion of the hydrate begins to decompose, the odour of triethylamine being distinctly perceptible. When the liquid which has been heated for some time at 55° is cooled, the solid obtained has the composition of the tetrahydrate. The tetrahydrate may also be formed from the hexahydrate by dehydration in a vacuum over phosphorus pentoxide. Thus 0·1090 gram of hexahydrate lost 0·0154 gram in two days, and the equivalent of the residue was found to be 220, the equivalent of the tetrahydrate being 219. That the hexahydrate is converted at 55° into a lower hydrate is made evident by the progressive lowering of the melting point of the solid which results on cooling. Thus a specimen which originally melted at 49·5° was found after being heated for five minutes to melt at 47°, and after thirty minutes' heating to melt at 43°.

The hexahydrate, like the tetrahydrate, dissolves in water with notable absorption of heat.

Tetrapropylammonium Hydroxide.

Tetrapropylammonium chloride was dissolved in methyl alcohol and mixed with the equivalent quantity of potassium hydroxide dissolved in the same solvent. An abundant precipitate of potassium chloride at once separated. The subsequent treatment was identical with that described under the preparation of tetraethylammonium hydroxide. The aqueous solution finally obtained did not crystallise after standing for a week in a vacuous desiccator over phosphorus pentoxide, and even on prolonged exposure to a temperature of $-20°$ showed no sign of solidification. A portion of this liquid, which had approximately the composition of a heptahydrate, was sealed in an evacuated tube with phosphorus pentoxide, and gently warmed for some time. On cooling in a freezing mixture, the liquid now partly crystallised, but the crystals disappeared when the temperature rose to that of the room. However, by rapid filtration through an asbestos filter surrounded by a good freezing mixture, it was found possible to separate the crystals from the mother-liquor. The crystals melted at the room temperature, and the liquid formed by their fusion was found to contain 2 per cent. of potassium chloride. Making allowance for this impurity, it was ascertained that 0·315 gram of the hydroxide required 38·5 c.c. of $N/40$ HCl for neutralisation, corresponding to an equivalent of 327. The heptahydrate of tetrapropylammonium hydroxide has the equivalent 329, so that in all probability the crystals consisted of the heptahydrate. The liquid from which the crystals separated had practically the same composition. Attempts to prepare a lower hydrate by dehydration were unsuccessful.

Trimethylsulphine Hydroxide.

An aqueous solution of trimethylsulphine hydroxide was prepared from trimethylsulphine chloride and potassium hydroxide according to the method already described, except that the temperature at which the distillation was conducted did not exceed 40°. The solution obtained, which had approximately the composition of an octahydrate, could not be made to crystallise in a freezing mixture, and even after slight warming in a vacuous tube over phosphorus pentoxide showed no signs of crystallisation at −20°, although it then had a composition intermediate between that of a pentahydrate and a tetrahydrate. Further attempts at dehydration and crystallisation were unsuccessful, owing to the ease with which the base decomposed.

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CLXIX.—para-*Toluidine Monohydrate.*

By JAMES WALKER and HEATHER HENDERSON BEVERIDGE (Carnegie Research Scholar).

IN the course of an investigation on the conductivity of the salts of certain bases, it was found necessary for comparison to determine the conductivity of *p*-toluidine hydrochloride. We were surprised to find that, according to the mode in which the solution was prepared, consistently different results were obtained. When the hydrochloride was purified by recrystallisation from water or from methyl alcohol, the conductivity results agreed with those obtained by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 323). When, on the other hand, the base itself was recrystallised from aqueous alcohol and a weighed amount dissolved in the requisite volume of standard hydrochloric acid, the conductivity values were much higher, corresponding to a deficit of about 14 per cent. of the base, or a like excess of acid. Since the conductivity of the acid was correct, it was necessarily the toluidine which was at fault, although the melting point of the sample used was sharp, and practically that given in the ordinary works of reference. The inconsistency could be most readily explained by the assumption that *p*-toluidine crystallises from aqueous alcohol in the form of a hydrate. No mention of a hydrate is made in Beilstein's *Handbuch*, but we found that the existence of a hydrated form of the base had been indicated by Lewy (*Ber.*, 1886, **19**, 2728), who, however, did not pursue the subject further, but merely stated that the crystals obtained from aqueous solution effloresced when exposed to the air.

That the base crystallised from aqueous alcohol as a hydrate could be seen on heating the dry crystals in a test-tube. As the temperature approached 40°, a film of moisture formed on the cold walls of the tube, and when the melting point was reached the liquid produced was plainly not homogeneous, globules of water being apparent in the bulk of the fluid.

The conductivity numbers indicated that the substance had approximately the composition of a monohydrate, but considerable trouble was experienced in obtaining a sample suitable for analysis, on account of the readiness with which the hydrate effloresces and loses water in a desiccator, or even when exposed to the air under ordinary conditions. By adopting the following device, however, which is of general applicability in the preparation of hydrates, we succeeded in obtaining specimens with a constant amount of water. The somewhat moist crystals of the hydrate were exposed in a closed space to the action of a large quantity of the anhydrous base, which served as dehydrating agent. The anhydrous substance is in equilibrium with the pressure of water vapour afforded by the lowest hydrate, but will absorb water from any substance which has a higher vapour pressure than this. Consequently the adherent moisture is completely removed by the anhydrous base, but the water of hydration of the lowest hydrate (in the present case the monohydrate) remains unabsorbed. In general terms, a hydrate can be completely dried, without being decomposed, by the dehydrating action of the next lower hydrate, the lowest hydrate of all being prepared by the dehydrating action of the anhydrous substance.

A sample of the substance dried in this way lost nothing to fresh anhydride after twenty-four hours' exposure, but on complete dehydration over calcium chloride and solid potassium hydroxide it lost 14·6 per cent. of its weight. In carrying out the complete dehydration quantitatively, it is necessary to strew the desiccator loosely with finely-divided *p*-toluidine in order that there may be no loss in the weighed quantity by vaporisation of the *p*-toluidine which it contains. The loss actually found corresponded closely with that demanded by the formula of a monohydrate, C_7H_9N,H_2O, namely, 14·4 per cent.

Elementary analysis confirmed this result:

0·1502 gave 0·3700 CO_2 and 0·1210 H_2O. C = 67·10; H = 8·95.
0·1265 „ 0·3105 CO_2 „ 0·1025 H_2O. C = 66·94; H = 9·00.
0·2275 „ 22·1 c.c. moist nitrogen at 15° and 771 mm. N = 11·55.
0·2089 „ 19·1 c.c. „ „ 12·5° „ 776 mm. N = 11·04.
C_7H_9N,H_2O requires C = 67·20; H = 8·80; N = 11·20 per cent.

The hydrate, then, which crystallises from a solution of *p*-toluidine in water or in aqueous alcohol at the ordinary temperature contains one molecule of water. It does not differ greatly in appearance from the anhydrous substance as crystallised from a non-aqueous solvent, nor is the difference in behaviour on melting, when the operation is carried out as usual in a capillary tube, at all striking. The melting point of the pure anhydrous base, as determined by the ordinary method, is 43·5°; when heated slowly, the hydrate shows signs of liquefaction at 38°, but does not properly melt until 42·5° is reached. When a closed tube containing the anhydrous base is plunged into water at 42°, there is incipient liquefaction on the upper portion of the walls of the tube, but the bulk of the substance does not melt; the hydrate, on the other hand, melts completely under the same conditions. In presence of water, the hydrate melts at a little below 42°. The difference in behaviour of *p*-toluidine hydrate when heated in an open and in a closed capillary is no doubt due to the loss in the first case of water of hydration as the heating progresses. In the ordinary laboratory atmosphere, the hydrate loses its water of crystallisation at a rate depending on the surface exposed and on the fineness of the crystals. The anhydrous base, on the other hand, is slowly converted into the hydrate when exposed to an atmosphere saturated with water vapour. The spontaneous dehydration of the hydrate may be readily observed under the polarising microscope. If a drop of aqueous-alcoholic solution is allowed to evaporate on the slide, the lozenge-shaped crystals of the hydrate may be seen to break up rapidly into numerous small crystals of the anhydrous base, the original outline of the larger hydrate crystals remaining unchanged until vaporisation of the *p*-toluidine itself destroys it.

A series of measurements of the vapour pressure of the hydrate at different temperatures was made in a Bremer-Frowein tensimeter. The pressure over the hydrate is almost entirely due to water vapour, as the vapour pressure of *p*-toluidine at its melting point does not exceed 1 mm. of mercury. For convenience of manipulation, the tensimeter was provided with a stop-cock on a bridge between the two limbs of the gauge, and the vertical tubes from the bulbs were not sealed, but were furnished with stoppers. Values for copper sulphate pentahydrate were obtained with this tensimeter which approximate closely to those given by Frowein (*Zeitsch. physikal. Chem.*, 1887, **1**, 11). One of the bulbs was charged with a mixture of anhydrous *p*-toluidine and *p*-toluidine monohydrate, and the other was charged with phosphorus pentoxide. For low temperatures, bromonaphthalene was used in the gauge, and for higher temperatures mercury. The results, expressed in millimetres of mercury, are given in the subjoined table:

Vapour Pressure of p-*Toluidine Monohydrate.*

Temperature ...	5°	11°	18°	20°	25°	28°	30°	32°	34°	36°	37°
Pressure.........	3·0	5·0	9·0	10·5	15·7	20·0	22·5	26·5	29·5	33·0	36·0
Vapour pressure of water	6·5	9·8	15·4	17·4	23·5	28·1	31·5	35·3	39·5	44·2	46·7

It is somewhat remarkable, in view of these values for the vapour pressure of the hydrate, that the substance should be efflorescent under ordinary laboratory conditions, for, in general, the pressure of water vapour in the atmosphere is greater than the vapour pressure of the hydrate. A special experiment showed that the hydrate rapidly lost weight when the pressure of water-vapour in the atmosphere was 8 mm. and the pressure registered in the tensimeter 6 mm. In ten hours under these conditions, the percentage of water in the exposed solid had sunk from 14 to 8. Possibly this abnormality is due to the volatility of the base itself, although it was found that the loss in weight of the anhydride when exposed to the air is much less than the loss of weight of the hydrate under the same conditions.

The vapour pressures registered for *p*-toluidine monohydrate are about 10 per cent. greater than those found by Frowein (*loc. cit.*, p. 14) for zinc sulphate heptahydrate. In order to ascertain if the behaviour of *p*-toluidine hydrate corresponded with these relative numbers, a portion of the pure hydrate was enclosed in a glass-box with a weighed quantity of zinc sulphate crystals having the average composition $ZnSO_4,6\cdot6H_2O$. It was found that the *p*-toluidine hydrate very slowly lost weight, and that the hydrated zinc sulphate experienced a corresponding gain. The behaviour of these hydrates in presence of each other is therefore in accordance with the values of the vapour pressure derived from the tensimeter experiments.

Dilatometric observations were made for the purpose of determining if any definite temperature of transition existed below the melting point of the hydrate. The dilatometer used was of the ordinary van't Hoff type, but for convenience in filling and handling, the capillary stem was bent into U-form close to the bulb. The dilatometer was charged with the solid hydrate and the bulb then filled with a saturated aqueous solution of the base. Readings were taken, at intervals of a few degrees, from 4° up to the melting point, but no discontinuity in the expansion was observed. Similarly, on cooling from just below the melting point to the ordinary temperature, the progress of the contraction with fall of temperature was perfectly regular. From these experiments, it would appear, therefore, that in presence of water the hydrate is stable up to the point at which it passes into a saturated solution of *p*-toluidine in water and a saturated solution of water in liquid *p*-toluidine.

This being the case, it was to be expected than anhydrous *p*-toluidine would unite with water to form the hydrate at all temperatures up to the "melting point" of the hydrate. To test this conclusion, a dilatometer was charged with anhydrous *p*-toluidine and rapidly filled with a saturated solution of the base, the whole apparatus during the process of filling being immersed in a thermostat at 41·0°. After the solid and solution came into contact, contraction at once occurred and continued for about an hour. As the temperature throughout the experiment remained constant, and since a special experiment showed that no difference in solubility could be detected when solutions were rapidly brought to the saturation point by anhydride and hydrate respectively, the contraction could only be attributed to the process of hydration. When the temperature was raised to 41·7°, the hydrate gradually liquefied with a corresponding expansion in the dilatometer. Up to the melting point, then, the anhydride unites with water to form the monohydrate.

When the finely-divided anhydrous base is brought into contact with a saturated aqueous solution of *p*-toluidine in a calorimeter, a rise of temperature is observed extending over about an hour, the heat evolved being approximately 20 calories per gram of base.

On the assumption that the heat of hydration is constant, it is possible by means of van't Hoff's formula:

$$Q = \frac{4{\cdot}6\ T_1 T_2}{T_1 - T_2} \log_{10} \frac{r_1}{r_2}$$

to calculate the heat of hydration, Q, from the ratio, r, of the dissociation pressure of water over the hydrate to the vapour pressure of pure water at the same temperature. The result of this calculation gives the heat of hydration equal to about 29 cal. per gram of *p*-toluidine. This value is greater than that found directly, but in consideration of the fact that the base became hydrated very slowly, and that the vapour pressures over the hydrate are not those of water only, the approximation may be deemed sufficient.

An attempt was made by Walker (*Zeitsch. physikal. Chem.*, 1890, **4**, 193) to calculate the heat of fusion of *p*-toluidine from the angle at which the solubility curves of the solid and liquid intersect at the melting point. This led to the value 44·5 cal. per gram instead of 39 cal. as directly determined. It was not then suspected that the solubility of the solid substance actually determined was that of the hydrate and not of the anhydrous base, but in view of the results given in the present paper, it is obviously the solubility of the hydrate which was measured. The calculation therefore should lead to an approximate value for the heat of fusion of the hydrate. This would be 39 + 25 = 64 cal. per gram of anhydrous base if we take a mean value for the heat of hydration. The calculated number 44·5 cal. is by no means in close accordance with this value.

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CLXX.—*The Production of Orcinol Derivatives from the Sodium Salt of Ethyl Acetoacetate by the Action of Heat.*

By JOHN NORMAN COLLIE and EDWIN RODNEY CHRYSTALL.

THE production, by means of a simple reaction, of benzene derivatives from fatty compounds is always of interest, and, as it had been noticed that by the action of heat on a mixture of ethyl acetoacetate and sodium ethoxide a compound was formed which gave the orcinol reaction with chloroform and sodium hydroxide, the substance was thought to be worth while investigating. That orcinol itself is formed from diacetylacetone, and dimethylpyrone in the presence of alkalis has already been noticed (J. N. Collie and W. S. Myers, Trans., 1893, **63**, 122). The amount produced, however, is very small. D. S. Jerdan (Trans., 1899, **75**, 808) has also obtained orcinol derivatives from ethyl acetonedicarboxylate.

The preparation of the condensation product of ethyl acetoacetate is easily carried out by heating ethyl acetoacetate with enough sodium ethoxide to convert about one-third of it into the sodium salt. The amounts usually employed were 78 grams of ethyl acetoacetate and 4·6 grams of sodium dissolved in 50 c.c. of absolute alcohol. The mixture was then heated in a distilling flask, ethyl acetate and alcohol distilled over, and the residue in the flask became deep orange and very viscous. After cooling, hydrochloric acid was added, when a crystalline substance mixed with some oil separated. The solid compound was washed with alcohol and dried. The yield of crude product was usually between 7 and 8 grams. It was purified by recrystallisation from benzene, from which it separated in long, colourless needles melting at 168—169°. On analysis:

C = 63·0, 62·8, 63·1* ; H = 5·1, 5·2, 5·4*.

$(C_8H_8O_3)_n$ requires C = 63·2 ; H = 5·2 per cent.

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* The authors wish to express their indebtedness to Miss E. K. Ewbank for the analyses marked with an asterisk in this pape .

The molecular weight was determined by the depression of the freezing point of benzene; the numbers 296* and 320 were obtained:

$C_{16}H_{16}O_6$ requires M.W. = 304.

The compound is soluble in sodium hydroxide with a bright yellow colour, which, however, becomes much less intense on warming; by addition of acid to the solution, a yellow, amorphous substance of high molecular weight is precipitated. This substance is peculiarly sensitive to faintly alkaline solutions, yielding a purple colour which is destroyed by excess of alkali or acid. When a solution of the substance in alcohol is added to acetic acid, or distilled water, or distilled water and carbon dioxide, its colour is yellow; strong alkalis give a pale yellow colour; but if any of the following substances be added to the alcoholic solution, namely, London tap water, sodium bicarbonate, calcium bicarbonate, lime water, sodium acetate, or even a large excess of sodium acetate and some acetic acid, then the purple colour is developed.

The compound $C_{16}H_{16}O_6$ may be evaporated to dryness with the strongest ammonia, leaving the unchanged substance. When boiled with acetic anhydride, no acetate is produced.

A mixture of nitric and sulphuric acids acts with great violence on the compound, but no nitro-derivative could be obtained.

With bromine, however, it gives a crystalline *bromo*-derivative. The bromination was carried out in acetic acid solution; on the addition of water, a yellow, crystalline compound separated. This was purified by solution in hot alcohol to which a few drops of hydrochloric acid had been added; otherwise decomposition of the compound with separation of free bromine ensues. It melts at 182·5° and on analysis gave the following numbers:

C = 35·3*, 35·4*, 35·9*; H = 3·1*, 3·6*, 3·0*; Br = 44·6*, 45·0*.

$C_{16}H_{15}O_6Br_3$ requires C = 35·4; H = 2·8; Br = 44·2 per cent.

When the compound $C_{16}H_{16}O_6$ is boiled with barium hydroxide solution, alcohol, barium acetate, and barium carbonate are formed. In one experiment, one gram was boiled for some time with excess of barium hydroxide solution, and the resulting barium carbonate after washing and decomposing with hydrochloric acid yielded 150 c.c. of carbon dioxide; this corresponds to two molecules of carbon dioxide from one of the compound $C_{16}H_{16}O_6$.

The action of hot 93 per cent. sulphuric acid was next tried. Five grams of the substance were mixed with 10 c.c. of the acid and heated. At about 130°, effervescence of carbon dioxide began, and at 140° a brisk evolution of gas occurred, the temperature being finally raised to 160°. The original substance dissolved in the sulphuric acid with a deep orange colour which soon disappeared when the mixture was heated. The products of the reaction were poured into water, the resulting precipitate being collected, washed with water, and dried. A further small amount was obtained by neutralising the acid filtrate with solid sodium carbonate.

In another experiment, the amount of carbon dioxide evolved was measured; one gram yielded 78 c.c. of carbon dioxide, which corresponds to the evolution of one molecule of carbon dioxide from one molecule of the compound $C_{16}H_{16}O_6$. The solid product of the reaction crystallised from alcohol in small, colourless needles which melt at 250° and contain water of crystallisation. On analysis:

$H_2O = 8{\cdot}3^*, 8{\cdot}5^*, 8{\cdot}7^*$.

$C_{11}H_{10}O_3,H_2O$ requires $H_2O = 8{\cdot}6$ per cent.

$C = 69{\cdot}2, 69{\cdot}0, 69{\cdot}2$; $H = 5{\cdot}4, 5{\cdot}6, 5{\cdot}4$.

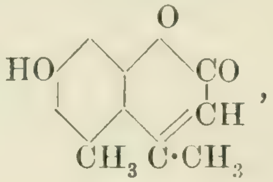
$C_{11}H_{10}O_3$ requires $C = 69{\cdot}2$; $H = 5{\cdot}4$ per cent.

A molecular weight determination was made by the lowering of the boiling point of an alcoholic solution:

Found: M.W. = 196, 196, and 197.

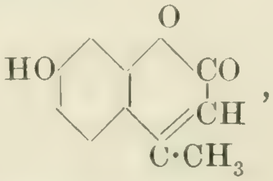
$C_{11}H_{10}O_3$ requires M.W. = 190.

Finally, the compound was identified with dimethylumbelliferone, obtained by the condensation of orcinol with ethyl acetoacetate, by von Pechmann and Cohen (*Ber.*, 1884, **17**, 2188). These authors have given the following formula to the compound:



I.

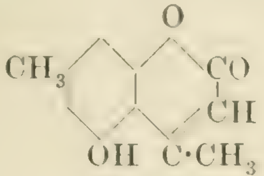
but did not prove the constitution of the substance, merely inferring it from the constitution of condensation products of ethyl acetoacetate with other phenols. One of these, namely, the condensation product of resorcinol with ethyl acetoacetate, has been well studied, and undoubtedly has the constitution:



but its reactions are somewhat different.

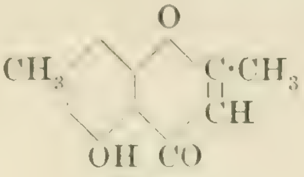
Reagent.	*Resorcinol Compound.*	*Orcinol Compound.*
Sulphuric acid	Blue fluorescence.	No fluorescence.
Sodium hydroxide.	Faintly yellow solution, blue fluorescence.	Intense yellow solution, no fluorescence.

Ethyl acetoacetate might, however, condense with orcinol differently, for instance:



Lactone.
II.

or



Pyrone.
III.

That the compound possesses the lactone formula was easily proved by the fact that it forms salts with bases. Two grams were boiled with barium hydroxide solution, using a large amount of water, the excess of barium was precipitated by carbon dioxide, and the hot solution filtered; on cooling, a *barium* salt crystallised out. On analysis, it was found to contain Ba = 25·0; $(C_{11}H_{11}O_4)_2Ba$ requires Ba = 24·8 per cent.

If the substance had been a pyrone, no such compound would have been produced.

To distinguish between the formula I, assigned to the compound by von Pechmann and Cohen, and formula II was found to be more difficult; but as the compound behaves so differently from the resorcinol compound when treated with either sodium hydroxide or sulphuric acid, and also as it gives such an intense yellow colour with the former reagent, it seems highly probable that formula II is the one that best expresses its molecular structure.

Several experiments were tried to decide this point. The compound was boiled with excess of sodium ethoxide in the hope that perhaps a simpler orcinol derivative might be formed, but only the unchanged substance could be separated from the products of the reaction. Potassium and sodium hydroxides dissolve the substance with a deep yellow colour which mostly disappears on heating, but on the addition of acid the original compound is reprecipitated. Even on fusion with potassium hydroxide at 180—200°, only the original substance and a little orcinol could be separated from the products of the reaction.

Oxidation with potassium permanganate took place at once in the cold, but only oxalic acid could be detected in the oxidation products. The compound $C_{11}H_{10}O_3$ when heated with acetic anhydride gave a quantitative yield of the acetate, $C_{11}H_9O_3(C_2H_3O)$; it was recrystallised from alcohol and melted at 198° (von Pechmann and Cohen give 195°). On analysis:

C = 66·5, 66·8; H = 5·6, 5·3.

$C_{13}H_{12}O_4$ requires C = 67·2; H = 5·2 per cent.

The *methyl ether* was prepared by the action of methyl sulphate. It crystallises in fine, white needles melting at 146°. It is insoluble in sodium hydroxide, except after prolonged boiling. On analysis:

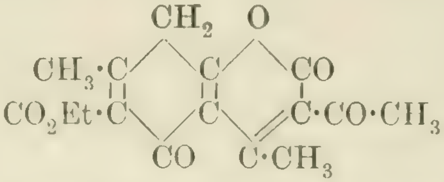
$C = 70{\cdot}4$; $H = 5{\cdot}9$.

$C_{11}H_9O_3{\cdot}CH_3$ requires $C = 70{\cdot}6$; $H = 5{\cdot}9$ per cent.

The oxidation of this compound by potassium permanganate was also tried, but no oxidation products could be isolated.

The action of hot sulphuric acid of about 93 per cent. was found to result in merely the removal of the methyl group, and the original compound $C_{11}H_{10}O_3$ was formed.

From the above reactions and decomposition products of the original compound $C_{16}H_{16}O_6$, a possible formula can be assigned to it, namely:



It is not a true orcinol derivative until after treatment with sulphuric acid, and does not contain a hydroxyl group. It does, however, give a nitrogenous compound when treated with hydroxylamine, but as condensation also occurs in the alkaline solution the compound formed was non-crystalline and could not be purified sufficiently for analysis.

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CLXXI.—*Derivatives of the Multiple Keten Group.*

By JOHN NORMAN COLLIE.

IN the present paper, the author wishes to call attention to the manner in which the group $\cdot CH_2{\cdot}CO\cdot$ (a group which he wishes to call the "*Keten*" group) can be made to yield by means of the simplest reactions a very large number of interesting compounds; the chief point of interest being that these compounds belong to groups largely represented in plants.

The syntheses of organic compounds in the laboratory, as chemists know, are almost entirely different from those used by the living plant (compare Meldola, *Chemical Synthesis of Vital Products*, Vol. I., p. 7). Moreover, the photosyntheses which take place in plants have at present no parallel in the laboratory. Regarding the production of the chief compounds in plants, the celluloses, the starches, and the sugars, at present we know but little.

Usher and Priestley (*Proc. Roy. Soc.*, 1906, **77**, *B*, 369, and **78**, 318) have clearly shown that the action of light on carbon dioxide, together with water and chlorophyll, gives only hydrogen peroxide, formaldehyde, formic acid, and oxygen, but that in order to build up starches and celluloses from carbon dioxide and water, it is absolutely necessary that healthy protoplasm should also be present. If therefore living protoplasm is one of the factors necessary for this synthesis, then the ordinary synthetical operations used by the organic chemist never can be sufficient to produce starches and celluloses. Also it is probable that the simpler organic compounds found in plants are produced by a degradation of these starches and celluloses. Again, possibly the reactions which produce them are also as different from the ordinary reactions used by the organic chemist, as the production from dextrose on the one hand, of alcohol and carbon dioxide by means of yeast, and, on the other, of oxalic acid by means of nitric acid.

In plants, the initial reaction, brought about by the combined effect of light and living protoplasm, is firstly to build up molecules of the very highest molecular complexity, from which afterwards the simpler compounds can be formed. In the laboratory, the chemist starts with the same material, but is only able to ascend step by step towards these degradation products produced in the plants. Although, however, the actual reactions taking place in the plant are different from those in the laboratory, still much may be done by studying, in the laboratory, reactions which might quite conceivably occur in plants, such as those involving hydration, dehydration, oxidation, reduction, polymerisation, and condensation at as near the ordinary temperature as possible. Moreover, the effect on these reactions of faintly acid or alkaline solutions is worth while investigating.

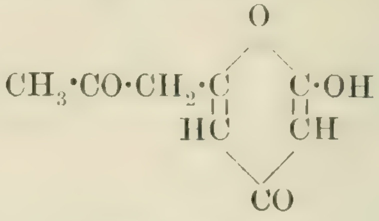
For many years, the author has had this object in view, and he drew attention to some of these ideas fourteen years ago (Trans., 1893, **63**, 329). The compounds which condense or polymerise most easily are the aldehydes and ketones, and by means of them carbon atoms can most easily be linked to carbon atoms. It was then pointed out "how easily the acetyl group condenses with itself" with the formation of such compounds as:

$H\cdot CH_2\cdot CO\cdot OH$, Acetic acid.
$H[CH_2\cdot CO]_2\cdot OH$, Diacetic acid.
$H[CH_2\cdot CO]_3\cdot OH$, Triacetic acid.
$H[CH_2\cdot CO]_4\cdot OH$, Tetra-acetic acid.

All these substances are compounds of the group $\cdot CH_2\cdot CO\cdot$, or keten group with water. It is these compounds and others which can be produced from them by addition or loss of water or of carbon dioxide, or of a ketene group, that the author proposes to call derivatives of the "multiple keten" group. For instance:

$H[CH_2\cdot CO]_4\cdot OH - H_2O =$

Tetra-acetic acid.



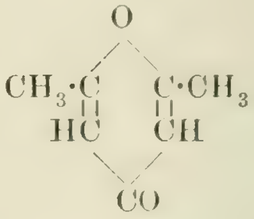
Dehydracetic acid.

$H[CH_2\cdot CO]_4\cdot OH - CO_2 = H[CH_2\cdot CO]_3\cdot CH_3$

Tetra-acetic acid. Diacetylacetone.

$H[CH_2\cdot CO]_3\cdot CH_3 - H_2O =$

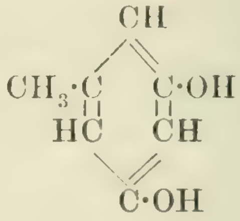
Diacetylacetone.



In acid solution. Dimethylpyrone.

$H[CH_2\cdot CO]_3\cdot CH_3 - H_2O =$

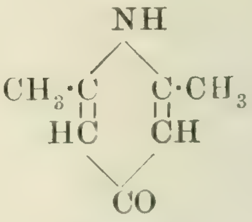
Diacetylacetone.



In strong alkaline solution. Orcinol (in small quantity).

$H[CH_2\cdot CO]_3\cdot CH_3 + NH_3 - 2H_2O =$

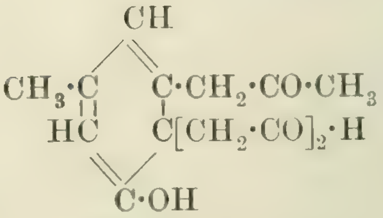
Diacetylacetone



Lutidone.

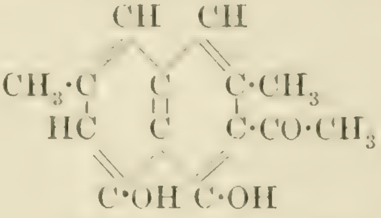
$2H[CH_2\cdot CO]_3\cdot CH_3 - H_2O =$

Diacetylacetone



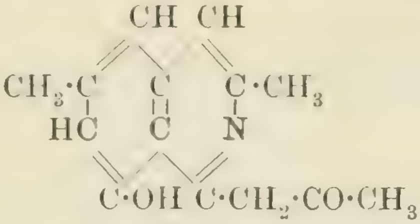
In faintly alkaline solution. Benzenoid compound.

This benzenoid compound when dissolved in strong aqueous potassium or sodium hydroxide loses another molecule of water, giving a naphthalene derivative:



Naphthalenoid compound

The benzenoid compound when treated with ammonia at the ordinary temperature gives an *iso*quinoline derivative:



*iso*Quinoline compound.

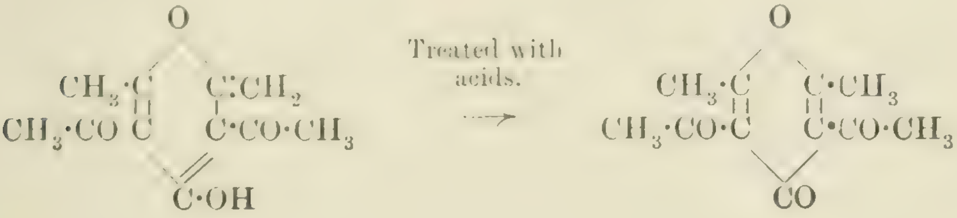
The ease with which all these condensations occur is most remarkable, as is also the diversity of the compounds produced.

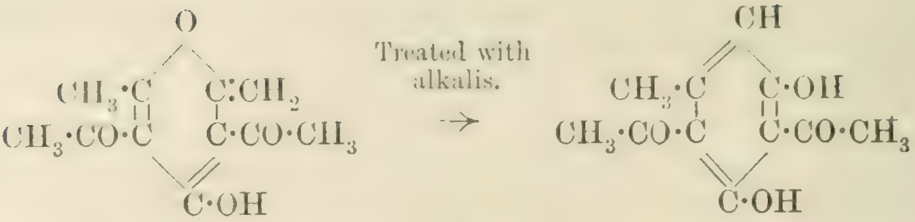
The chief reason for the chemical reactivity of these compounds and why they often give quite different condensation products in alkaline or in acid solution is that they all possess the grouping the properties of which are well exemplified in ethyl acetoacetate, namely,

$$\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot .$$

According to circumstances, this group may react either in the ketonic or enolic condition, and acids and alkalis are the reagents which are best suited for bringing about this change in the molecular structure of the substance, a change which is usually expressed by a shifting in the position of the double bond.

Amongst the derivatives of the multiple keten group, an interesting example is to be found in the compound obtained by the action of acetyl chloride on the sodium salt of diacetylacetone (Trans., 1904, 85, 975). The substance is not a true pyrone derivative, neither is it a benzene compound, but hydrochloric acid converts it entirely into diacetyldimethylpyrone, whilst sodium hydroxide transforms it into diacetylorcinol.





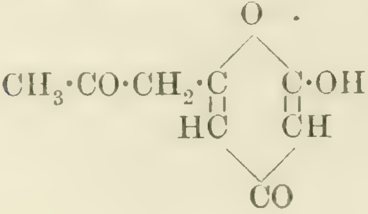
Several other instances might be given, for instance, diacetylacetone with acids gives dimethylpyrone, whilst with strong alkalis orcinol is formed in small quantity together with acetone and sodium acetate. The tendency of the acid is to produce:

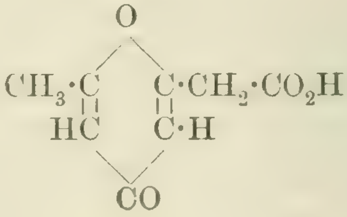
$$CH_3\cdot C(OH):CH\cdot CO\cdot CH:C(OH)\cdot CH_3\,;$$

and of alkalis to give:

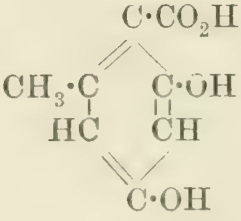
$$CH_3\cdot C(OH):CH\cdot C(OH):CH\cdot C(OH):CH_2.$$

Dehydracetic acid also shows this difference. When treated with sulphuric acid (Trans., 1907, **91**, 787), it partly changes to a pyronecarboxylic acid (I), whilst with alkalis the isomeric orcinolcarboxylic acid (II) is formed.



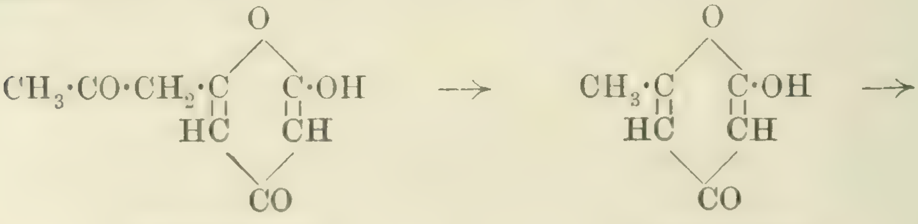


I.



II.

The chief action, however, of strong hydrating agents is to produce simpler substances. For instance, dehydracetic acid, diacetylacetone, dimethylpyrone, &c., give acetic acid and acetone when boiled with strong aqueous sodium hydroxide. But with different strengths of sulphuric acid, the down-grade hydrolysis can be better followed, for instance:



Dehydracetic acid. Triacetic lactone

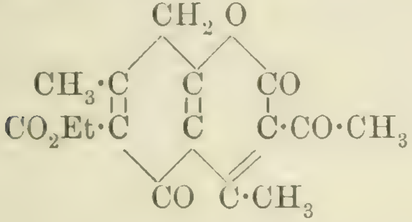
$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3+CO_2$$

Acetylacetone.

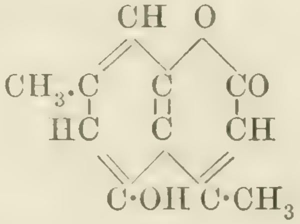
and finally the acetylacetone breaks down into acetone and acetic acid.

In the case where, however, there is a stable ring formation, such as in the diacetylorcinol mentioned above, strong hydrating agents merely split off the side keten groups and orcinol is left.

Another point of interest in these substances is the ease with which carbon dioxide is eliminated from them. The simplest case of this kind is, of course, acetoacetic acid. But dehydracetic acid also suffers this loss when converted into tetra-acetic acid by hydrolysis. The isomeric pyronecarboxylic acid decomposes so easily that considerable loss occurs during crystallisation, the solution effervescing through loss of carbon dioxide. Orcinolcarboxylic acid also is very unstable, easily losing carbon dioxide. It has already been shown how, from the combination of two molecules of diacetylacetone in concentrated or in slightly alkaline solution, more complicated derivatives of the multiple keten group can be produced. This is found to be the case also when the sodium salt of ethyl acetoacetate is heated (see preceding paper); the compound $C_{16}H_{16}O_6$ being partly a benzenoid and partly a pyrone compound (I):



I.

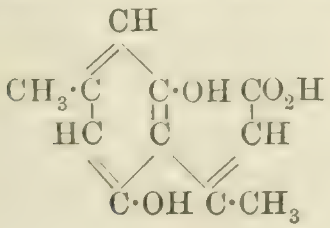


II.

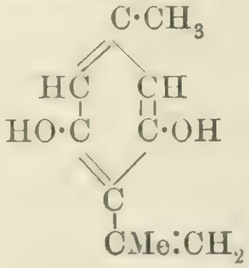
It has also been pointed out how, when this substance is hydrolysed by heating with sulphuric acid, a simpler substance, dimethylumbelliferone (II), is produced.

The properties of this complex derivative (for the production of which from ethyl acetoacetate, only two simple reactions are needed) are of especial interest. Although colourless itself, with sodium hydroxide it gives a brilliant yellow compound. This is to be expected, as it is a "benzopyrone" compound, and therefore belongs to the same type as many of the yellow dyes.

Moreover, this brilliant yellow compound when warmed with more sodium hydroxide becomes nearly colourless, and the solution when acidified and extracted with ether gives the free acid (I):



I.



II.

This acid undergoes two interesting changes:

(1) On heating, it yields carbon dioxide and a substance (II) which has an odour resembling that of thymol; also when heated with phosphorus and iodine in a sealed tube traces of cymene are formed.

(2) When it is allowed to remain in a faintly alkaline solution in contact with air, the solution gradually absorbs oxygen, becoming a dark cherry-red. This is due to the formation of a dye which possesses properties similar to brazilin. The dye may be obtained from the acidified solution by extraction with ether, in which it is soluble. It then consists of a yellowish-red powder, but it could not be obtained pure owing to the fact that it could not be made to crystallise. Like brazilin, it dissolves in water with a yellow colour, which is at once changed to cherry-red by alkalis. It is decolorised by sodium hydroxide and zinc dust, but the colour is at once restored by shaking the colourless solution with air. Analysis gave:

$C = 57{\cdot}2$; $H = 4{\cdot}5$.

A molecular weight determination gave M.W. = 470.

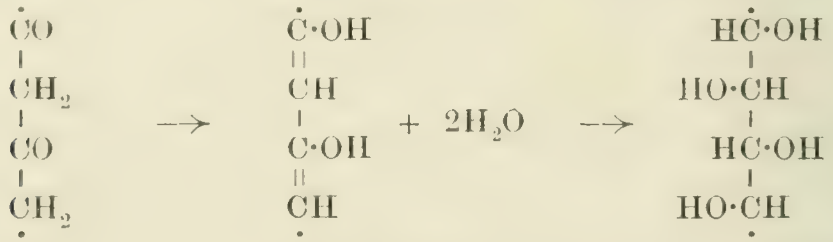
$C_{22}H_{22}O_{11}$ requires $C = 57{\cdot}3$; $H = 4{\cdot}7$ per cent. M.W. = 462.

Silk and cotton can only be dyed by this substance after mordanting; with alum, a brownish-red colour is produced.

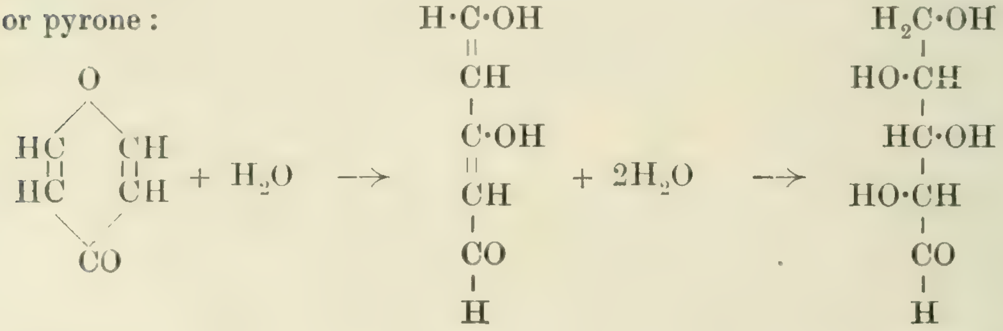
Whether the substance has a molecular structure similar to brazilin has not yet been ascertained, but it is not difficult to account for such a substance either on the lines of the formula of Kostanecki or that of Perkin.

In conclusion, the close relationship of these pyrone or keten compounds to the sugars, and through them to the starches and celluloses, might be pointed out. The whole question is one of hydrolysis.

Taking two keten groups:

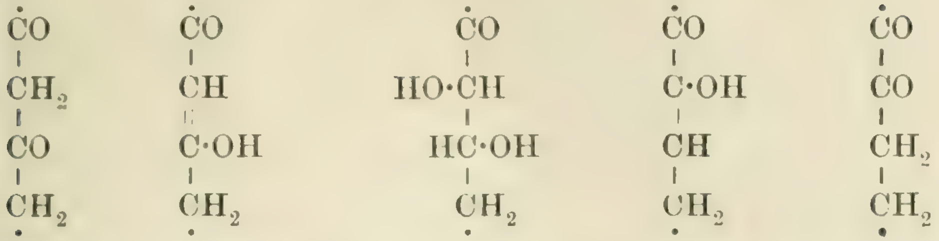


or pyrone:



Pyrone. Pentose.

whilst if the hydration were to take place in another way :

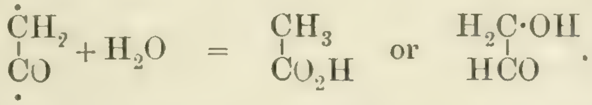


$$\begin{array}{ccccc} \overset{\bullet}{CO} & \overset{\bullet}{CO} & \overset{\bullet}{CO} & \overset{\bullet}{CO} & \overset{\bullet}{CO} \\ | & | & | & | & | \\ CH_2 & CH & HO\cdot CH & C\cdot OH & CO \\ | & \| & | & | & | \\ CO & C\cdot OH & HC\cdot OH & CH & CH_2 \\ | & | & | & | & | \\ \underset{\bullet}{CH_2} & \underset{\bullet}{CH_2} & \underset{\bullet}{CH_2} & \underset{\bullet}{CH_2} & \underset{\bullet}{CH_2} \end{array}$$

then, in a long chain of keten groups, or hydrated keten groups (such as are undoubtedly present in the starches and celluloses), there would be an accumulation of oxygen towards one end of the chain, that is, carbon dioxide would be evolved; whilst at the other end, hydrogen or $\cdot CH_2 \cdot$ groups would predominate.

This might be offered as an explanation of the formation of fats and oils, and the production of carbon dioxide. That some such change can occur is plainly seen by the formation of alcohol, carbon dioxide, succinic acid, and glycerol from dextrose by fermentation. It is the living ferment that can effect this particular kind of hydrolysis.

Free keten reacting with water gives acetic acid, but perhaps under the influence of healthy protoplasm, glycollaldehyde and its polymerides might be produced :



$$\begin{array}{c}\overset{\bullet}{CH_2}\\ |\\ \underset{\bullet}{CO}\end{array} + H_2O = \begin{array}{c}CH_3\\ |\\ CO_2H\end{array} \text{ or } \begin{array}{c}H_2C\cdot OH\\ |\\ HCO\end{array}.$$

It has already been pointed out by the author (Trans., 1905, **87**, 1548) that when $\cdot CH_2 \cdot$ groups are combined with carbon monoxide by means of the silent electric discharge, combination occurs and a keten group results. Moreover, that the $\cdot CH_2 \cdot$ group easily combines with itself forming complex chains of $\cdot CH_2 \cdot$ groups was also noticed, and what was of considerable interest was the fact that certain definite nuclei of these $\cdot CH_2 \cdot$ groups appeared to be more stable than others. These nuclei are represented by C_{10} and C_{15} or C_{16}. Such nuclei are found in the terpenes and in the fatty acids.

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CLXXII.—*Racemisation by Alkali as Applied to the Resolution of* r-*Mandelic Acid into its Optically Active Isomerides.*

By Alex. McKenzie and Hermann August Müller, Ph.D.

Some three years ago, one of us (Trans., 1904, **85**, 1249) attempted to effect the asymmetric synthesis of mandelic acid from benzoylformic acid by the aid of *l*-menthol, the method adopted being to reduce *l*-menthyl benzoylformate by aluminium amalgam, saponify the product, and then completely remove the menthol from the resulting mixture. It was anticipated at the time that an asymmetric synthesis would be brought about in accordance with the scheme: $C_6H_5 \cdot CO \cdot CO_2H \rightarrow C_6H_5 \cdot CO \cdot CO_2 \cdot C_{10}H_{19} \rightarrow C_6H_5 \cdot CH(OH) \cdot CO_2 \cdot C_{10}H_{19} \rightarrow C_6H_5 \cdot CH(OH) \cdot CO_2H$. The mandelic acid, obtained by this method, was, however, invariably optically inactive, although there was distinct evidence that the reduction of the benzoylformate had actually proceeded asymmetrically. That the reduction product in such a case is a mixture of unequal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate, containing a slight preponderance of the latter, was indicated by a determination of its specific rotation, which gave a value numerically higher than that of the partially racemic *l*-menthyl *r*-mandelate; the latter ester, which is readily formed from the *r*-acid, would have been produced if the reduction had proceeded symmetrically. The failure to realise the asymmetric synthesis of mandelic acid was found to be due to the racemising effect exercised by the alkali during the saponification of the ester mixture. It was noted in this connexion that partial racemisation takes place with remarkable ease when *l*-menthyl *l*-mandelate is saponified by alcoholic potassium hydroxide; *l*-mandelic acid is easily converted into this ester, but the *l*-acid cannot be regenerated from it free from the *r*-isomeride, no matter under what conditions the saponification is conducted. The behaviour of *l*-menthyl *d*-mandelate on saponification is similar.

Marckwald and McKenzie showed that, when *r*-mandelic acid is heated at 155° for one hour with *l*-menthol, the unesterified acid is lævorotatory, and on this observation a method was based for resolving optically inactive compounds into their active components differing in principle from any of Pasteur's classical methods (*Ber.*, 1899, **32**, 2130; 1900, **33**, 208; 1901, **34**, 469; Marckwald and Meth, *Ber.*, 1905, **38**, 801). The conclusion was drawn that the velocity of formation of *l*-menthyl *d*-mandelate is greater than that of *l*-menthyl *l*-mandelate during the heating of the *r*-acid with *l*-menthol, and it was found subsequently by direct measurements of the velocity of saponification of these esters that the *d*-mandelate is the more readily saponifiable of the two (McKenzie and Thompson, Trans., 1907, **91**, 789). The fractional saponification of *l*-menthyl *r*-mandelate was also studied (*Ber.*, 1899, **32**, 2130; Trans., 1904, **85**, 378). This ester is obtained by esterifying *r*-mandelic acid by *l*-menthol as completely as possible according to the Fischer-Speier method; it is a partially racemic ester, which is easily prepared in a state of uniformity, since under ordinary conditions it may be crystallised unchanged and is, accordingly, not resolved on crystallisation. When saponified by an excess of alkali, it yields the *r*-acid. When an insufficiency of alkali was used, the fractional saponification method of Marckwald and McKenzie gave, on almost every occasion, a dextrorotatory acid.

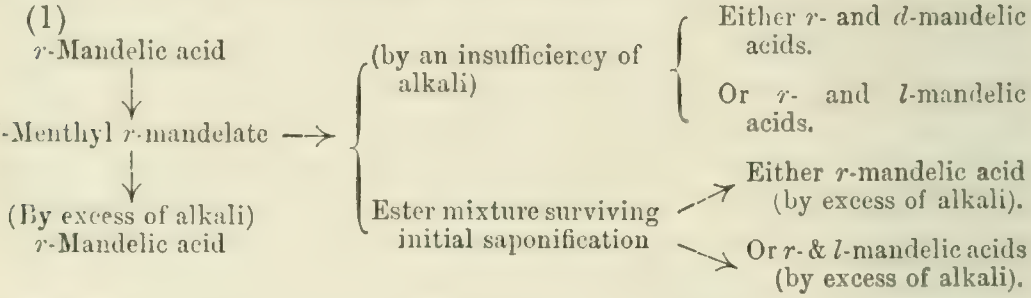
This result is normal. An alcoholic solution of the partially racemic ester contains equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate. Since the former is the more readily saponifiable of the two, the fractional saponification of the partially racemic ester by alcoholic potassium hydroxide might be expected to give a *dextrorotatory* potassium salt. On two separate occasions, however, a *lævorotatory* salt was obtained, and, at the time, the reason of this was not clear. The racemisation phenomena, however, subsequently observed during the saponification of menthyl and bornyl esters by alkali (McKenzie and Thompson, Trans., 1905, **87**, 1004) threw light on this problem, and many unsuccessful attempts were accordingly made to obtain the conditions under which a lævorotatory potassium salt would result on the fractional saponification of the partially racemic ester in question. These attempts have been continued with success, and the results are embodied in the present paper.

When the fractional saponification is conducted in concentrated solution under the conditions recorded in the experimental part, a lævorotatory potassium salt is formed, and from this a specimen of the pure *l*-acid may be isolated. It is shown that, as a product of the fractional saponification of *l*-menthyl *r*-mandelate in alcoholic solution, either a dextrorotatory or a lævorotatory acid may be obtained from the same weight of ester and using the same weight of alkali.

In each case, in addition to the fractional saponification, racemisation by alkali of the active potassium salt formed occurs. The formation of the dextrorotatory potassium salt is easily accounted for, the racemisation phenomena being in this case of secondary importance. The formation of the lævorotatory salt, however, is due to the racemisation being pronounced, and is explained as follows. Shortly after the saponification has started, we have a mixture of (1) *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate, the latter being in excess; (2) potassium *r*-mandelate; (3) alkali; (4) ethyl alcohol, and (5) menthol. If no racemisation had taken place, (2) would have consisted of a mixture of potassium *d*-mandelate and potassium *l*-mandelate with an excess of the former; the alkali is, however, strong enough at this stage to cause the formation of an inactive potassium salt. As the saponification proceeds, the concentration of the alkali becomes less and less, and its tendency to cause racemisation is also diminishing, until towards the end of the operation it is negligible. On the other hand, the ratio of *l*-menthyl *l*-mandelate to *l*-menthyl *d*-mandelate in the unsaponified portion is gradually increasing, so that the potassium salt formed, instead of being inactive as towards the start of the action, now becomes lævorotatory. The explanation is simply that, in the initial stages of the saponification, the racemisation caused by the alkali is marked, and becomes less and less as the saponification proceeds. A similar interpretation had been previously advanced to account for the behaviour of *l*-menthyl *dl*-phenylethoxyacetate on fractional saponification (Trans., 1905, **87**, 1004).

The following transformations, in which racemisation by alkali plays a part, have accordingly been realised:

(1)


r-Mandelic acid
l-Menthyl *r*-mandelate
(By excess of alkali)
r-Mandelic acid
(by an insufficiency of alkali)
Either *r*- and *d*-mandelic acids.
Or *r*- and *l*-mandelic acids.
Ester mixture surviving initial saponification
Either *r*-mandelic acid (by excess of alkali).
Or *r*- & *l*-mandelic acids (by excess of alkali).

(2) By conducting the fractional saponification of *l*-menthyl *r*-mandelate in such a manner that a dextrorotatory potassium salt is formed as the product of the initial saponification, and then saponifying the surviving ester mixture by an excess of alkali in such a manner that the racemising effect of alkali is brought into action, the change *r*-mandelic acid ⟶ *r*-mandelic acid and *d*-mandelic acid may be accomplished.

(3) By heating *r*-mandelic acid with *l*-menthol, removing the unesterified acid by shaking the ethereal solution of the reaction product with aqueous sodium carbonate, and then saponifying the residual ester mixture with an excess of alkali, the change *r*-mandelic acid ⟶ *r*-mandelic acid and *l*-mandelic acid may be brought about (Marckwald and McKenzie, *loc. cit.*). This transformation can also be effected by conducting the fractional saponification of *l*-menthyl *r*-mandelate in such a manner that a lævorotatory potassium salt is formed as the product of the initial saponification and then saponifying the surviving ester mixture by an excess of alkali. In the latter case, the racemising effect of alkali may or may not be caused to be pronounced.

It should be observed that these changes are not examples of asymmetric synthesis, inasmuch as the starting point is *r*-mandelic acid, a compound which already contains an asymmetric carbon atom.

Similar transformations may also be effected by aid of *l*-borneol. When *l*-bornyl *r*-mandelate is saponified by an insufficiency of potassium hydroxide, it generally gives a lævorotatory potassium salt (Trans., 1904, **85**, 378; 1905, **87**, 1004) differing in this respect from *l*-menthyl *r*-mandelate and behaving abnormally, since *l*-bornyl *d*-mandelate is more quickly saponified than *l*-bornyl *l*-mandelate (Trans., 1907, **91**, 789). It is, however, shown in the present paper that it is possible to choose such conditions that the racemising action of the alkali is minimised and a dextrorotatory potassium salt is formed. Accordingly, when *l*-bornyl *r*-mandelate is submitted to fractional saponification, either a dextrorotatory or a lævorotatory potassium salt can be obtained at will.

EXPERIMENTAL.

The Change r-*Mandelic Acid* ⟶ r-*Mandelic Acid and* l-*Mandelic Acid.*

l-Menthyl *r*-mandelate was prepared as previously described (Trans., 1904, **85**, 378). The ester (145 grams) was heated to melting at the temperature of a boiling-water bath, and 46·3 c.c. of ethyl-alcoholic potassium hydroxide (1 c.c. = 0·45 KOH), which is about three-fourths of the amount necessary for complete saponification, were warmed and quickly added. The mixture was shaken vigorously, and the reaction was accompanied by a considerable development of heat. The product was heated at 100° under a reflux apparatus for five hours, but, since after twenty-four hours more at the ordinary temperature the liquid was still alkaline, the heating was continued for two hours longer, at the end of which time the liquid was neutral. The ethyl alcohol was then distilled off, an excess of water added to the residue, the precipitated ester mixture and menthol drained off, the filtrate extracted with ether, and the ethereal extract added to the ester mixture and menthol. The usual precautions were taken to ensure that the aqueous solution of potassium salt contained neither ester nor menthol, the solution having been evaporated to a small bulk and again extracted with ether, when no residue was obtained on removal of the ether. The aqueous solution of the potassium salt was acidified by mineral acid and extracted with ether (not quantitatively), when 33 grams of a mixture of *r*- and *l*-mandelic acids were obtained. A determination of the specific rotation of this acid mixture in ethyl alcohol gave the result:

$$l = 2,\ c = 10{\cdot}57,\ \alpha_{D}^{14} - 1{\cdot}15^{\circ},\ [\alpha]_{D}^{14} - 5{\cdot}4^{\circ}.$$

The mixture was then treated in the manner already described by

Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130) in order to separate a specimen of the pure *l*-acid. The bulk of the *r*-acid was first removed by crystallisation from water in such a manner that all the active acid remained in the mother liquors. The latter were then converted into magnesium salt, which was fractionated so that as much magnesium *r*-mandelate as possible was separated, the mother liquors again retaining the active product. On conversion of the latter into cadmium salt, a small amount of cadmium *r*-mandelate was removed, and the filtrate decomposed by hydrogen sulphide. In this manner, about 1·1 grams of nearly pure acid were obtained, which, on crystallisation from water, gave a specimen of the pure *l*-acid melting at 131·5—132·5°, and having the following rotation in aqueous solution:

$$l = 2,\ c = 0{\cdot}9620,\ \alpha_D^{17}\ -3{\cdot}01°,\ [\alpha]_D^{17}\ -156{\cdot}4°.$$

The mixture of residual esters and menthol was freed from ether and the complete saponification carried out with a large excess of alkali in such a manner that the racemising action of the alkali was pronounced. The mixture was melted, and a warm solution of 80 grams of potassium hydroxide in 200 c.c. of ethyl alcohol was added quickly. After the vigorous reaction had subsided, the mixture was heated for two hours at the temperature of a boiling-water bath, and the subsequent manipulation conducted as before. The mandelic acid, obtained in this manner, was only slightly lævorotatory, giving, in ethyl-alcoholic solution, $\alpha_D\ -0{\cdot}14°$ for a 10 per cent. solution in a 2-dcm. tube.

Two other experiments may be quoted in order to show how an alteration of conditions affects the activity of the product from the final saponification. To the melted ester (9·7 grams) was added 2·7 c.c. of ethyl-alcoholic potassium hydroxide (1 c.c. = 0·112 KOH) and the mixture heated at 100° for one hour. The aqueous potassium salt, obtained in the usual manner, gave, on evaporation to the bulk, necessary to fill a 2-dcm. tube, the value $\alpha_D\ -0{\cdot}84°$, whilst the resulting mandelic acid mixture (1·5 grams) gave in ethyl-alcoholic solution:

$$l = 2,\ c = 10{\cdot}24,\ \alpha_D^{18}\ -0{\cdot}81°,\ [\alpha]_D^{18}\ -4{\cdot}0°.$$

The residual ester mixture was then saponified by an excess of alkali, about five times more than was necessary. To the warm ester mixture was added 15 c.c. of ethyl alcoholic potassium hydroxide (1 c.c. = 0·4536 KOH), but the subsequent heating at 100° was continued in this case for fifteen minutes only, with constant shaking. The mandelic acid mixture (3 grams), obtained in the usual manner, gave the following rotation in ethyl-alcoholic solution:

$$l = 2,\ c = 7{\cdot}234,\ \alpha_D^{8}\ -2{\cdot}33°,\ [\alpha]_D^{8}\ -16{\cdot}1°.$$
$$l = 2,\ c = 10{\cdot}15,\ \alpha_D^{10}\ -3{\cdot}25°,\ [\alpha]_D^{10}\ -16{\cdot}0°.$$

In another experiment, the same amount of ester was used as before, the same amount of alkali added under the same conditions, and the heating continued for four hours. The aqueous solution of potassium salt, when evaporated to the bulk necessary to fill a 2-dcm. tube, gave in this case α_D $-0·91°$, whilst the acid mixture gave in ethyl-alcoholic solution:

$$l=2,\ c=10·4,\ \alpha_D^{18·5}\ -1·04°,\ [\alpha]_D^{18·5}\ -5·0°.$$

The ester mixture was then saponified at the ordinary temperature and in dilute solution with slightly more than the calculated amount of alkali. The mixture of esters and menthol was dissolved in 100 c.c. of ethyl alcohol, and 50 c.c. of ethyl-alcoholic potassium hydroxide, containing 1·4 grams of alkali, was added, with constant stirring, during the space of two hours. After forty-eight hours, the solution was only slightly alkaline. The resulting mandelic acid mixture (3 grams) gave in ethyl-alcoholic solution:

$$l=2,\ c=5·21,\ \alpha_D^{14}\ -1·25°,\ [\alpha]_D^{14}\ -12·0°.$$

The Change r-*Mandelic Acid* ⟶ r-*Mandelic Acid and* d-*Mandelic Acid.*

l-Menthyl *r*-mandelate (145 grams) was submitted to fractional saponification under conditions differing from those already given in the first experiment quoted in this paper. It is of importance to note that the weight of ester is the same as before, as also is the weight of alkali. The partially racemic ester was dissolved in 1500 c.c. of ethyl alcohol, and 500 c.c. of ethyl-alcoholic potassium hydroxide, containing 20·8 grams of alkali, was added, drop by drop, at the ordinary temperature within an interval of five hours, the solution being continuously stirred. In this manner, the racemising action of the alkali was reduced to a minimum. The solution was then allowed to remain for forty-eight hours at the ordinary temperature and was then neutral. The ethyl alcohol, unsaponified esters, and menthol were then removed as usual, and the aqueous solution of potassium salt, when decomposed by mineral acid, gave a mandelic acid mixture having the following rotation in ethyl-alcoholic solution:

$$l=2,\ c=10,\ \alpha_D^{14}\ +0·76°,\ [\alpha]_D^{14}\ +3·8°.$$

The yield of acid was 55 grams. The *r*-acid was removed in a manner similar to that already described for the isolation of the *l*-acid from the lævorotatory acid mixture. Finally, 1·3 grams of nearly pure *d*-acid were obtained which, on crystallisation from water, gave a specimen of pure *d*-mandelic acid, melting at 132—133°, and showing the following rotation in aqueous solution:

$$l=2,\ c=1·065,\ \alpha_D^{14}\ +3·29°,\ [\alpha]_D^{14}\ +154·4°.$$

After the ether had been expelled from the solution of menthyl esters and menthol, which survived the initial saponification, the product was completely saponified, using the same weight of alkali as in the first experiment quoted, namely, 80 grams. The resulting acid was slightly lævorotatory, giving $\alpha_D -0{\cdot}12°$ for a 10 per cent. ethyl-alcoholic solution in a 2-dcm. tube.

In the case of the final saponification, it is possible, by minimising the racemising effect of the alkali, to obtain an acid mixture with a specific rotation in aqueous solution as high as $-15°$. In the example just quoted, the racemising action of the alkali was caused to be pronounced in order to make the change *r*-mandelic acid ⟶ *r*-mandelic acid and *d*-mandelic acid more obvious.

The Normal Fractional Saponification of l-*Bornyl* r-*Mandelate.*

As has already been pointed out in the introduction, *l*-bornyl *r*-mandelate generally behaves abnormally on fractional saponification giving a lævorotatory potassium salt, the residual ester mixture under the conditions formerly employed having given an inactive potassium salt. By varying the experimental conditions, a dextrorotatory acid mixture may be obtained from the initial saponification and a lævorotatory acid mixture from the final saponification. Both saponifications were conducted at the ordinary temperature and in dilute solution.

Thirty grams of *l*-bornyl *r*-mandelate (Trans., 1905, **87**, 1004) were dissolved in 1000 c.c. of ethyl alcohol and partially saponified by the addition, during the space of one hour, of 200 c.c. of ethyl-alcoholic potassium hydroxide; the amount of alkali in the latter solution was one-half of that necessary for complete saponification. The action was conducted with constant stirring at the ordinary temperature. After four hours at the ordinary temperature, the neutral solution was freed from ethyl alcohol, borneol, and residual esters, and gave a dextrorotatory acid mixture:

$l=2$, $c=7{\cdot}85$, $\alpha_D^{18} +0{\cdot}21°$, $[\alpha]_D^{18} +1{\cdot}3°$ (in ethyl-alcoholic solution).

The mixture of residual esters and borneol was dissolved in 500 c.c. of ethyl alcohol and completely saponified by the addition, within the space of one hour, of 200 c.c. of ethyl-alcoholic potassium hydroxide containing slightly more than the calculated amount of alkali. After the solution had remained for twenty-four hours at the ordinary temperature, it was manipulated in the usual manner, the resulting mandelic acid being lævorotatory:

$l=2$, $c=9{\cdot}98$, $\alpha_D^{11} -0{\cdot}99°$, $[\alpha]_D^{11} -5{\cdot}0°$ (in ethyl-alcoholic solution).

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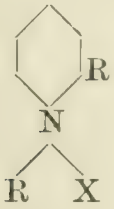
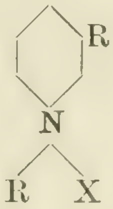
CLXXIII.—*The Optical Activity of Cyclic Ammonium Compounds.*

By FRANK BUCKNEY, B.A., and HUMPHREY OWEN JONES.

IT has now been clearly established in a large number of cases that a quinquevalent nitrogen atom of the type NabcdX can give rise to optical activity due to the absence of a plane of symmetry in the molecule.

Certain compounds which contain a quinquevalent nitrogen atom forming part of a ring, as previously stated by one of us (Trans., 1903, **83**, 1405), contain no plane of symmetry, and so should be optically active. Accepting the current views as to the configuration of the nitrogen atom, *α*- and *β*-substituted pyridinium compounds, (I) and (II), quinolinium compounds (III), and tetrahydroquinolinium compounds (IV) should all exist in optically active forms. Several compounds of the above type were prepared and their resolution attempted in the usual way, but without success (*loc. cit.*, 1415). Thus 1-methyl-*α*-picolinium *d*-camphorsulphonate and *d*-bromocamphorsulphonate, methylkairolinium-1-acetate *d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-methyl-1-ethyltetrahydroquinolinium *d*-bromocamphorsulphonate and 1-benzyl-1-ethyltetrahydroquinolinium *d*-camphorsulphonate were submitted to a long process of fractional crystallisation without separating them into the two constituents which were expected to be present.


I.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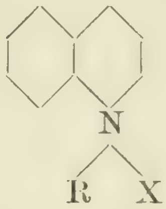
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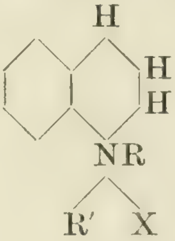
IV.

Up to the present time, the only case in which the activity of a cyclic compound is attributed to a nitrogen atom is that of the ethylenedikairolinium salts examined by Wedekind (*Ber.*, 1905, **38**, 1841). These salts, however, show certain abnormalities which have not yet been explained. Compounds in which activity is partly due to an asymmetric nitrogen atom have been prepared by Scholtz (*Ber.*, 1904, **37**, 3627) from *d*-coniine.

It seemed desirable to make further attempts to obtain active cyclic compounds in which the activity was due to an asymmetric nitrogen atom, and, if possible, to throw some light on the difficulties which have hitherto prevented the resolution of such compounds.

The present paper contains an account of an examination of a number of compounds which, theoretically, should give rise to optical activity. Quinoline compounds could, in no case, be shown to exhibit activity, and in one case only could it be proved conclusively that a tetrahydroquinoline compound was optically active.

It is possible that in the quinoline compounds the existence of a double linking between the nitrogen and carbon atoms and the consequent possibility of oscillatory changes occurring at this point may prevent such compounds from exhibiting activity. At present, however, taking into account the quite exceptional difficulties which have been encountered in the resolution of tetrahydroquinoline derivatives, in which there can be no such effect, the evidence available is insufficient to justify the suggestion of possible explanations.

In all, eight tetrahydroquinoline derivatives of the necessary constitution, $C_9H_{10}\colon NRR_1X$, have been examined, but in one case only, namely, that of the allylkairolinium salts, have we succeeded in obtaining conclusive evidence of optical activity due to the nitrogen atom.

It is at present impossible to understand what causes these compounds to be so much more difficult to resolve than other quinquevalent nitrogen compounds in which the nitrogen does not form part of a ring.

Methylquinolinium d-*camphorsulphonate* was prepared in the usual way from the corresponding iodide; after several recrystallisations from ethyl acetate, it melted at 118°, and gave values for the molecular rotatory power in aqueous solution of 48·5—50°, values approximating to that for the acid ion, namely, 51·7°.

Benzylquinolinium iodide was found to crystallise well and to melt at 135°. The d-*camphorsulphonate* was prepared and recrystallised from ethyl acetate nine times, when it was found to melt at 120° and gave $[M]_D$ 48·4°.

Allylkairolinium iodide * was prepared and converted into the d-*bromocamphorsulphonate* in the usual way; this was found to be readily soluble in acetone and in ethyl acetate. After repeated recrystallisation from a mixture of acetone and toluene, the rotatory power of the less soluble fraction was found to diminish until it became constant, when $[M]_D = 195°$ approximately. The more soluble portion was purified by dissolving it in acetone, precipitating fractionally with light petroleum, and then evaporating the solution to dryness; in this way, the salt was obtained with $[M]_D = 320°$. This was the *d*-base *d*-acid salt, but it was evidently impure.

It was observed that when the salt was allowed to separate slowly from its solutions in ethyl acetate and toluene, two distinct kinds of crystals were deposited, one kind being short, transparent prisms, whilst the other consisted of long, silky needles. (This behaviour has been observed in other cases, notably that of phenylmethylallyl*iso*propylammonium *d*-camphorsulphonate, but the difference was found to be merely one of habit.) On separating these two kinds of crystals roughly by hand, a fairly simple process, it was found that the short prisms were the *l*-base *d*-acid salt, whilst the long needles were the *d*-base *d*-acid salt. Each sort of crystal was then recrystallised separately, when the *l*-base *d*-acid salt was obtained pure and the *d*-base *d*-acid salt fairly pure.

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* A preliminary note on the activity of this compound has already appeared. Buckney, *Proc. Camb. Phil. Soc.*, 1907, **14**, 177.)

l-*Allylkairolinium* d-*bromocamphorsulphonate.*—The less soluble salt crystallises in small, colourless, transparent prisms melting at 164°:

0·1916 gave 0·3889 CO_2 and 0·1141 H_2O. C = 55·4 ; H = 6 62.

$C_{23}H_{32}O_4NBrS$ requires C = 55·4 ; H = 6·43 per cent.

The following determinations of rotatory power were made on several samples, some of which had been purified simply by crystallisation and others by crystallisation after a rough mechanical separation :

0·109 in 11·81 of solution in a 2-dcm. tube gave α_D 0·75 ; hence $[\alpha]_D$ 40·6° and $[M]_D$ 202°.

0·133 in 12·03 solution in a 2-dcm. tube gave α_D 0·88° ; hence $[\alpha]_D$ 39·8° and $[M]_D$ 198°.

0·161 in 17·12 of solution in a 2·2-dcm. tube gave $[\alpha]_D$ 0·81° ; hence $[\alpha]_D$ 39·16° and $[M]_D$ 195°.

Taking the value of $[M]_D$ for the acidic ion as 270°, we get $[M]_D$ for the basic ion about − 75° to − 77°.

d-*Allylkairolinium* d-*bromocamphorsulphonate* was obtained fairly pure by recrystallising the long needles which had been separated mechanically, and consisted of long, silky needles melting at 153·5° :

0·1419 gave 0·2890 CO_2 and 0·855 H_2O. C = 55·5 ; H = 6·69.

$C_{23}H_{23}O_4NBrS$ requires C = 55·4 ; H = 6·43 per cent.

The following determinations of rotatory power were made on different preparations :

0·1678 in 17·46 solution in a 2·2-dcm. tube gave α_D 1·46° ; hence $[\alpha]_D$ 69·05° and $[M]_D$ 343·9°.

0·100 in 11·87 of solution in a 2-dcm. tube gave α_D 1·16° ; hence $[\alpha]_D$ 68·8° and $[M]_D$ 342·9°.

Taking $[M]_D$ 270° for the acid ion, we get $[M]_D$ + 73·4° for the basic ion.

The iodide was not precipitated by the addition of concentrated potassium iodide solution to the solution used for the determination of rotatory power, but a small quantity of the crystalline iodide was deposited when a concentrated solution of the bromocamphorsulphonate was mixed with excess of concentrated potassium iodide solution. The quantity obtainable was not great enough to allow of trustworthy determinations of its rotatory power, which was also rendered the more difficult by the fact that the salt racemised very readily even in alcoholic solution. It was, however, observed that the solutions of iodides precipitated from the two different salts had opposite rotatory powers, and so proved that these salts contained the enantiomorphous bases. Thus 0·051 of the iodide precipitated from the less soluble bromocamphorsulphonate in 9·260 of alcohol solution in a 2-dcm. tube gave a_D $-0{\cdot}10°$ ($d = 0{\cdot}800$); hence $[\alpha]_D$ $-11{\cdot}3°$ and $[M]_D$ $-35{\cdot}7°$.

The evidence detailed above leaves no room for doubt that the two forms of allylkairolinium salts have been separated and that both are optically active and enantiomorphously related to one another, and so establishes the fact that an asymmetric nitrogen atom in a ring behaves normally.

Several other tetrahydroquinoline derivatives were examined and some of those already examined were re-investigated, but in no other case was any conclusive evidence of resolution obtained, although in several cases it will be seen that the values of $[M]_D$ for the salts do not agree very closely with that for the acid ion.

Benzylkairolinium d-*camphorsulphonate* was prepared from the iodide and was found to be readily soluble in acetone or ethyl acetate; it was therefore recrystallised repeatedly from a mixture of ethyl acetate and toluene and finally melted at 166—167°.

The rotatory powers of successive fractions were determined, and $[M]_D$ was found to vary from 49·7° to 52°, values almost identical with that for the acid ion, namely, 51·7°.

The iodide recovered from the camphorsulphonate was found to be quite inactive in alcoholic solution.

Benzylkairolinium d-*bromocamphorsulphonate* was prepared and recrystallised repeatedly from a mixture of ethyl acetate and toluene; it then melted at 176° and gave values of $[M]_D$ varying from 270° to 275°. The iodide recovered from this salt also was inactive.

Since it has frequently been found that salts which cannot be resolved at the ordinary temperature, owing to the fact that they are partially racemic, can be resolved at a higher temperature which is above the transition point of the double salt, it was thought possible that this end might be achieved in this case in the same way. The salt was therefore recrystallised from ethyl acetate and acetone in a water-oven. The value of $[M]_D$ was then found to be 279°.

It was also recrystallised from amyl acetate on a water-bath, and the value of $[M]_D$ was then 275° to 284° for different specimens, The iodide recovered from this salt was practically inactive, the greatest rotation ever observed being 0·03° in alcohol.

It has been shown that these ammonium compounds can be resolved by means of tartaric acid (Miss Homer, *Proc. Camb. Phil. Soc.*, 1907, **14**, ii, 196), and this method has subsequently been found to succeed in some cases where the camphorsulphonic acids had failed; the acid tartrate was therefore prepared by treating a solution of the base, obtained by acting on the iodide dissolved in alcohol and water with silver oxide, with the calculated quantity of tartaric acid and evaporating to dryness. The tartrate did not crystallise well from any solvents that were tried, and was purified by dissolving in alcohol and adding ether gradually until a turbidity was produced when the crystalline salt separated on standing. After repeating this process several times, the iodide was recovered and examined, but again it did not show any appreciable rotatory power.

Ethylkairolinium d-*camphorsulphonate* [the corresponding *d*-bromocamphorsulphonate had been examined previously (*loc. cit.*, 1417)] was prepared and recrystallised repeatedly from a mixture of acetone and toluene. It then melted at 70° and gave values of $[M]_D$ for successive fractions varying from 47° to 52°, so that no resolution had been effected.

n-*Propylkairolinium iodide* was prepared by heating kairoline and propyl iodide in molecular proportions in a sealed tube to 100° for some days, until the mixture had set to a solid mass; the iodide, which was readily soluble in alcohol, was recrystallised from a mixture of alcohol and ether, and was obtained in plates melting at 132—133°:

0·1423 gave 0·2562 CO_2 and 0·0790 H_2O. C = 49·0; H = 6·18.
$C_{13}H_{20}NI$ requires C = 49·2; H = 6·31 per cent.

The *d*-camphorsulphonate and the *d*-bromocamphorsulphonate were found to be crystalline, but the former was found to be very difficult to recrystallise from all the solvents available, and has not yet been examined.

The d-*bromocamphorsulphonate* is rather sparingly soluble in acetone or ethyl acetate, even when hot; after repeated recrystallisation from these solvents, it melted at 177—178°, and gave values for $[M]_D$ from 286° to 290°. It was also recrystallised from a mixture of alcohol and ethyl acetate, and was obtained in large, colourless, transparent prisms melting at 178—179°, and then gave $[M]_D$ 277—290°.

The iodide could not be recovered from solutions of the bromocamphorsulphonate.

The *platinichloride* was precipitated in beautiful, orange prisms, darkening at 210°, and melting with decomposition at 216°; these were, however, almost insoluble in all the organic solvents available, and so the compound could not be examined for rotatory power.

It is therefore doubtful whether any resolution has been effected in this case; it is, however, probable that there has been no resolution, since the propyl compound would probably have a rotatory power of much the same order of magnitude as the allyl compound.

These experiments are being continued, and other suitable compounds are also under examination.

The expenses of this investigation have been largely met by grants from the Government Grant Committee of the Royal Society, for which the authors are glad to make this grateful acknowledgment.

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CLXXIV.—*Some Double Ferrocyanides of Calcium, Potassium, and Ammonium.*

By JAMES CAMPBELL BROWN, D.Sc.

IN some modern text-books, solutions of calcium salts are said to form a precipitate on addition of ammonium chloride and potassium ferrocyanide. It was thought desirable to ascertain the composition of this precipitate and the conditions of its formation, and the investigation has led to a revision of, and addition to, our knowledge of double ferrocyanides.

Preparation of Potassium Calcium Ferrocyanide.

The salt, $K_2CaFeC_6N_6$, was prepared by mixing cold concentrated solutions of potassium ferrocyanide and calcium chloride in molecular proportions. The precipitate was washed in cold water and dried at 100°.

Analysis.—A weighed amount of the dried salt was gently ignited in a porcelain dish, treated with *aqua regia*, and evaporated several times with the same agent. The acid solution was filtered from the blue precipitate, which was washed, and the washings added to the filtrate. The clear filtrate was heated to boiling and made alkaline with ammonia. The ferric hydroxide was collected, redissolved, and again precipitated in order to remove all the potash, the filtrates being added to the original filtrate. This solution was then heated to boiling, and the calcium precipitated as oxalate and weighed as CaO. The filtrate from the calcium oxalate was evaporated to dryness, during which some iron still retained was precipitated; the dried residue was ignited gently to remove ammonium salts, dissolved in water, and the potassium was estimated as platinichloride. This is a tedious method, and not trustworthy, except as applied to calcium, because some potassium cyanide is lost by ignition, and because it is difficult to wash out the potash from the blue precipitate which is formed by treatment with *aqua regia*.

In later experiments, another method was adopted. A weighed portion of the salt was boiled with water and an excess of lead chloride. This results in the quantitative precipitation of lead ferrocyanide, the calcium and potassium passing into solution as chlorides. The solution was cooled and filtered from lead ferrocyanide and excess of lead chloride. The lead in the filtrate was precipitated by hydrogen sulphide, and in the solution, which was free from lead, the calcium was precipitated as oxalate and the potassium as platinichloride in the usual way. It was necessary to carry out the decomposition in neutral aqueous solution, because the presence of acid caused the decomposition of some of the ferrocyanide:

Found, $Ca = 11{\cdot}92$ and $12{\cdot}33$. $K = 23{\cdot}94$.
$K_2CaFeC_6N_6$ requires $C = 12{\cdot}12$; $K = 23{\cdot}68$ per cent.

As a check, the iron was determined with a mean result of 17·15, theory requiring 16·97 per cent. The salt, dried in the air, and then at 100°, showed no loss of water of crystallisation, and further drying at 120° produced no loss of weight. This salt must therefore be anhydrous. Moissan (*Traité de Chim. Min.*, iv, 429) quotes Marchand (*J. Ch. Medic.*, 1844, 20, 558) as attributing three molecules of water of crystallisation to this salt. Several specimens have been prepared, however, and none has contained water of crystallisation. It is white when pure, becoming slightly cream-coloured on exposure to light, and consists of small, quadratic prisms.

Preparation of Ammonium Calcium Ferrocyanide.

By treatment of the potassium calcium salt with an equivalent quantity of ammonium chloride, the ammonium was not substituted for potassium at the ordinary temperature.

(*a*) Concentrated solutions of calcium chloride and potassium ferrocyanide were mixed in molecular proportions, and the precipitate collected; to the filtrate, a large excess of ammonium chloride solution was added and the precipitate collected, washed with cold water, and dried.

(*b*) The precipitate of the potassium calcium ferrocyanide was boiled with water, and a large excess of ammonium chloride added. The precipitate now obtained was washed well with cold water and dried at 100°. The two precipitates obtained by methods (*a*) and (*b*) were found to be of identical composition, and yielded on analysis a practically constant quantity of ammonia, provided that a sufficient excess of ammonium chloride was employed. The potassium remained in the soluble portion. Comparatively small quantities of the ammonium calcium salt are obtained by methods (*a*) and (*b*).

(*c*) The salt was also obtained in larger amount by first preparing pure ammonium ferrocyanide and precipitating it by calcium chloride. The salt thus obtained agreed in composition with the precipitates obtained by methods (*a*) and (*b*) just mentioned. This salt is white when pure and fresh, and consists of minute, anhydrous, prismatic crystals. It becomes coloured by the action of light.

Analysis.—Ammonia was estimated by distilling a weighed portion of the salt with excess of potassium hydroxide, collecting the ammonia in standard sulphuric acid, and determining the excess of acid by standard sodium hydroxide, using litmus as indicator.

Analysis of the precipitate (*a*) and (*b*):

Found, $NH_4 = 12{\cdot}33$; $Ca = 14{\cdot}03$.

Analysis of precipitate (*c*):

Found, $NH_4 = 11{\cdot}79$ and $12{\cdot}11$. Mean $= 11{\cdot}95$.
$Ca = 13{\cdot}45$ and $14{\cdot}01$. Mean $= 13{\cdot}73$.
$(NH_4)_2CaFeC_6N_6$ requires $NH_4 = 12{\cdot}5$; $Ca = 13{\cdot}89$ per cent.

The salt loses no water of crystallisation either at 100° or at 120°; it is therefore anhydrous.

Determination of the Solubilities of Potassium Calcium Ferrocyanide and of Ammonium Calcium Ferrocyanide.

From 2 to 3 grams of the dry salt in each case were added to 500 c.c. of distilled water in a flask and agitated for about thirty-five hours by bubbling washed air through the mixture at a temperature of 15—17°. The solution, which was of a yellow colour, was then filtered, and 100 c.c. of the clear filtrate were weighed and evaporated to dryness; the residue was dried at 100° and weighed. In each case, the result was checked by determining the amount of calcium as oxalate in 250 c.c. of the solution; from this, the amount of salt dissolved was calculated, the percentage of calcium in the salt being known.

Potassium Calcium Ferrocyanide.—One hundred c.c. weighed 100·04 grams and yielded 0·0475 gram of residue. Consequently by evaporation it is found that:

100 c.c. dissolve .... 0·407 gram
By estimation of the calcium .... 0·412 ,,

Mean = 0·41 ,,

or 1 part of the salt dissolves in 244 parts of water at 15—17°.

Ammonium Calcium Ferrocyanide.—By evaporation it is found that:

100 c.c. dissolve .... 0·259 gram
By estimation of the calcium .... 0·257 ,,

Mean = 0·258 ,,

or 1 part of the salt dissolves in 388 parts of water at 15—17°.

As a qualitative test, it is manifestly desirable to form as much of the ammonium salt as possible, rather than the potassium salt; but under ordinary working conditions, the pure ammonium calcium ferrocyanide will not be the salt precipitated.

Experiments have shown that for each proportion of the reagents, potassium ferrocyanide, calcium chloride, and ammonium chloride, an equilibrium results, so that by greatly increasing the amounts of ammonium chloride the proportion of ammonium increases and the proportion of potassium decreases in the precipitated salt.

The following epitome of the results which have been obtained will bring out the principal points. The first four columns indicate the number of molecular proportions of the several salts which have been mixed, and column 5 shows the percentage of ammonium found in the precipitate.

Precipitates formed from Concentrated Solutions.

	1. Mol. $K_4FeC_6N_6$.	2. Mols. $CaCl_2$.	3. Mols. AmCl.	4. Mols. KCl.	5. % NH_4.
1.	1	2	9	–	8·85
2.	1	1	1	—	3·00
3.	1	1	2	—	4·27
4.	1	1	6	—	8·17

Precipitates formed from Dilute Solutions.

	1.	2.	3.	4.	5.
5. Precipitated hot	1	1	1	—	2·54
6. ,, cold	1	1	1	—	2·42
7. Precipitated by heating filtrate from 6	1	1	1	—	2·46
8.	1	1	2	—	4·46
9.	1	1	6	—	8·48
9B.	1	1	6	—	8·42
10.	1	1	12	—	10·24
11.	1	1	20	—	11·29
11B.	1	1	20	—	11·27

$(NH_4)_2CaFeC_6N_6$ yields $NH_4 = 12·5$ per cent.

Effect of adding varying quantities of Potassium Chloride.

	1. Mol. $K_4FeC_6N_6$.	2. Mol. $CaCl_2$.	3. Mols. AmCl.	4. Mols. KCl.	5 % NH_4.
12.	1	1	6	1	8·05
13.	1	1	6	2	7·41
14.	1	1	6	6	5·94

From experiments 5, 6, and 7, it is seen that the precipitate formed in the hot solution, that formed in the cold solution, and that formed on heating the filtrate from the cold solution are all practically identical. Experiments 12, 13, and 14, and many others, which it is needless to add to the epitome, show that by the presence of potassium chloride in the solution the amount of the ammonium present in the precipitated salt is decreased proportionally, but analyses of a number of the precipitates show that this is not due simply to substitution of potassium for ammonium and vice versa. The proportion of calcium is less than corresponds to Ca_2, and the salts are triple ferrocyanides of calcium, potassium, and ammonium.

In ordinary qualitative working, the best conditions for the test are to add approximately molecular proportions of potassium ferrocyanide to the calcium salt, a large excess of ammonium chloride, and to heat the mixture. A precipitate formed in this way from one molecular proportion each of calcium chloride and potassium ferrocyanide and six molecular proportions of ammonium chloride gave on analysis:

(I) Ca = 12·93; K = 8·25; NH_4 = 8·17. (II) Ca = 12·69; K = 8·13 per cent.

The figures in (I) would be given by a mixture containing 47·31 per cent. of calcium ferrocyanide, 19·46 per cent. of potassium ferrocyanide, and 32·23 per cent. of ammonia ferrocyanide.

A precipitate formed by mixing one molecular proportion each of calcium chloride and potassium ferrocyanide and twenty molecular proportions of ammonium chloride gave on analysis:

Ca = 12·39; NH_4 = 11·29, and a small proportion of potassium.

Here, ammonium has replaced some of the calcium as well as most of the potassium.

Precipitate No. 3 in the table, formed from one molecular proportion each of calcium chloride and potassium ferrocyanide and two molecular proportions of ammonium chloride, gave on analysis:

C = 12·77; K = 15·83; NH_4 = 4·27 per cent.

These figures would be given by a mixture containing 46·2 per cent. of calcium ferrocyanide, 37·1 per cent. of potassium ferrocyanide, and 16·7 per cent. of ammonium ferrocyanide.

Since the above was written, it appears that F. B. Dains (*J. Amer. Chem. Soc.*, 1907, **29**, 728) has attributed the formula :

$$K_2CaFe(CN)_6,4(NH_4)_2CaFe(CN)_6,2H_2O,$$

to "the product formed by precipitating a calcium salt with potassium ferrocyanide in the presence of a large excess of ammonium chloride or nitrate." The proportions of the different substances mixed together are not stated, and the precipitates were dried at 70°.

No doubt analytical figures approximating to the percentages in this formula will be obtained from precipitates prepared within some limits, but by varying more widely the proportions of the several salts it becomes quite clear that the precipitate varies as the result of mass action.

If the figures given on p. 1830 as the result of mixing one molecular proportion each of calcium chloride, potassium ferrocyanide, and six molecular proportions of ammonium chloride had been calculated on the same principle as Dains' calculation, they would have indicated the formula : $K_2CaFeC_6N_6,2(NH_4)_2CaFeC_6N_6$. The present author purposely refrained from writing such a formula, because a formula is apt to mislead the reader into thinking that the mixture is constant, which it is not.

The water shown in Dains' formula is obviously due to the salt having been dried at 70°.

By drying at a more appropriate temperature, the anhydrous character of the salt has been repeatedly confirmed.

I have to thank Mr. T. Callan, B.Sc., for his valuable assistance in carrying out the practical work and analyses.

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CLXXV.—*The Condensation of Acetaldehyde and its Relation to the Biochemical Synthesis of Fatty Acids.*

By HENRY STANLEY RAPER.

THE formation of fatty acids in animals, from carbohydrates, and the occurrence in natural fats, such as butter, of all the fatty acids containing an even number of carbon atoms, from two to twenty, suggest that these fatty acids are produced by the condensation of some highly reactive substance containing two carbon atoms and formed in the decomposition of sugar.

It has been suggested by Nencki that in the butyric fermentation of lactic acid, acetaldehyde, carbon dioxide, and hydrogen are first formed, and that two molecules of the acetaldehyde then unite to form butyric acid:

$$CH_3{\cdot}CH(OH){\cdot}CO_2H = CH_3{\cdot}CHO + CO_2 + H_2.$$
$$2CH_3{\cdot}CHO = C_3H_7{\cdot}CO_2H.$$

Magnus Levy (*Englemann's Archiv*, 1902, 365) and Leathes (*Problems in Animal Metabolism*, London, 1906) have extended this suggestion to explain the formation of the higher fatty acids. Their conclusions receive support from the fact that *n*-hexoic acid has long been known to be a regular product of the butyric fermentation, and it has already been shown in a former communication (*Proc. Physiol. Soc.*, 1907, xxiv) that *n*-octoic acid is also produced to a small extent. According to the hypothesis referred to, therefore, in the formation of fatty acids from dextrose, lactic acid is the first product, and on the decomposition of this into acetaldehyde, carbon dioxide, and hydrogen, condensation of the aldehyde occurs, leading to the formation of the higher acids.

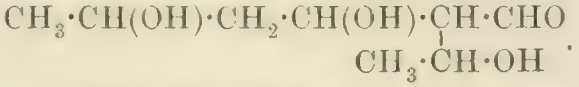
The chief difficulty in the acceptance of these views lies in the fact that all the previous work on the condensation of aliphatic aldehydes has shown that the products of condensation are aldehydes with branched, and not straight, chains (Lieben, *Monatsh.*, 1901, **22**, 289). This is due to the tendency of the aldehyde group of one molecule to condense with the α-carbon atom of the other molecule. Thus propaldehyde on condensation gives rise to β-hydroxy-α-methylvaleraldehyde and not to hexaldehyde:

$$2CH_3{\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}CHO.$$

But it must not be forgotten that Lieben's deductions have been confined to observations made on the condensation of aldehydes, such as acetaldehyde, propaldehyde, and valeraldehyde, which contain no hydroxyl groups; and, since when acetaldehyde condenses with itself the first product is necessarily β-hydroxybutyraldehyde (aldol), it is possible that the presence of the hydroxyl group in the β-position might influence the further course of the reaction, and conceivably lead to the production of an aldehyde with a straight chain.

The present paper deals with a study of this condensation, the first stage of which, namely, the formation of an aldehyde with eight carbon atoms from aldol, has been investigated. Previous observations on this subject are to be found in a paper by Wurtz (*Compt. rend.*, 1880, **91**, 1030), in which a substance, dialdane, $C_8H_{14}O_3$, is described as a product of the condensation of acetaldehyde under the influence of hydrochloric acid. The substance is regarded as possessing the constitution $CH_3\cdot CH(OH)\cdot CH_2\cdot CH{:}CH\cdot CH(OH)\cdot CH_2\cdot CHO$, but this formula is unsupported by evidence.

If the condensation of aldol followed the rule established by Lieben and his collaborators, then the first product of condensation should be $\beta\delta$-dihydroxy-α-ethanolhexaldehyde,



$$CH_3\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot \underset{CH_3\cdot CH\cdot OH}{\underset{|}{CH}}\cdot CHO\ .$$

By condensation under the influence of dilute potassium carbonate aldol has been found to yield, not this substance, but a hydroxyoctaldehyde with a straight chain. Unfortunately, this aldehyde has never been obtained quite pure, and on this account a more complete examination of its structure has had to be abandoned. Analyses made with the substance purified as far as was possible indicate that on condensation a molecule of water is eliminated with the formation of an inner anhydride and not of an unsaturated compound as is generally the case. Under the action of traces of mineral acid, two molecules of the substance lose a molecule of water, forming an aldehyde, $C_{16}H_{26}O_5$.

That the carbon atoms are in a straight chain in the condensation product has been proved by oxidising it to the corresponding acid and then reducing this by means of hydriodic acid. In this way, *n*-octoic acid was obtained, and identified by means of its amide and barium salt. α-Ethylhexoic acid, which would have been obtained at this stage had the condensation taken place according to Lieben's rule, has been prepared for comparison.

EXPERIMENTAL.

The aldol used in the experiments was prepared by the condensation of acetaldehyde in presence of 5 per cent. potassium carbonate solution (Orndorff and Newbury, *Monatsh.*, 1892, **13**, 516).

Condensation of Aldol.—As condensing agent, a 5 per cent. solution of potassium carbonate was used. One hundred grams of freshly prepared aldol were mixed with 100 c.c. of distilled water and the solution cooled in ice. Five grams of solid potassium carbonate were then added in small portions, the solution being kept below 10° during the process. When the potassium carbonate had completely dissolved, the solution was kept at a temperature of 13—14° until a yellow oil had separated at the bottom of the vessel. The time occupied was about sixty hours. The solution was now diluted to 800 c.c. with water, rendered slightly acid with hydrochloric acid, and the yellow, tarry substance separated. The filtrate was extracted with 200 c.c. of ether in order to separate a little of the tarry matter remaining in solution from the condensation product, which is much less soluble. Barium carbonate was now added to the solution to neutralise the free acid, and the whole was distilled in steam for three hours to remove unchanged aldol. As the condensation product is also volatile to a small extent, a little is lost in this process. The solution in the distilling flask was now concentrated to a syrup by evaporating the water under reduced pressure, and extracted with ether. After drying the ethereal extract over anhydrous copper sulphate, the ether was removed by distillation and a pale yellow, very viscous liquid remained. The yield was 35 per cent. of the aldol taken.

The substance decomposed when distilled under the ordinary as well as under reduced pressure. It did not give crystalline derivatives by the usual methods applicable to aldehydes, although it gave the usual aldehyde reactions. On warming with a trace of calcium chloride or mineral acid, or on heating alone for some time, it gave rise to a new compound, which, unlike the parent substance, was less soluble in hot water than cold.

The molecular weight was determined by the boiling point method. For this purpose, the substance was heated to 50° under diminished pressure in a stream of dry carbon dioxide to remove the last traces of ether and moisture. The substance so obtained gave a slight opalescence on dissolving in water, which increased on warming:

0·7121 in 9·05 of alcohol raised the boiling point 0·47°. M.W = 193.
0·7121 ,, 13·70 ,, ,, ,, 0·32°. M.W = 187.
$C_8H_{16}O_4$ requires M.W = 176. $C_8H_{14}O_3$ requires M.W = 158.

On analysis:

0·1706 gave 0·3833 CO_2 and 0·1347 H_2O. C = 61·28; H = 8·77.
$C_8H_{14}O_3$ requires C = 60·76; H = 8·86 per cent.
$C_8H_{16}O_4$,, C = 54·54; H = 9·09 ,,

These analytical results indicate that a molecule of water is eliminated in the process of condensation.

The high value obtained for the molecular weight is due to the presence of a substance derived from two molecules of the aldehyde, $C_8H_{14}O_3$, by the removal of water. This change, as stated above, takes place very readily on warming with a trace of calcium chloride or mineral acid, or merely by heating alone for some time. The new substance thus formed is very easily recognised by being much less soluble in hot water than cold; its cold aqueous solution immediately becomes milky on warming. On analysis:

0·2091 gave 0·4973 CO_2 and 0·1607 H_2O. C = 64·88; H = 8·54.
0·5250, in 7·37 of alcohol, gave an elevation of 0·28°. M.W. = 293.
0·5250 ,, 11·74 ,, ,, ,, 0·18°. M.W. = 286.
$C_{16}H_{26}O_5$ requires C = 64·43; H = 8·72 per cent. M.W. = 298.

It was found impossible to obtain a specimen of the condensation product quite free from this anhydride, the mere heating in a vacuum in order to dry the substance for analysis causing a certain amount of dehydration with consequent production of the anhydride. On this account, the analytical results can only be taken as approximately correct. When dissolved in acetic acid, the condensation product absorbed only a trace of bromine, so that it appears to be a saturated compound. It seems probable, therefore, that the water which is eliminated during condensation comes from two hydroxyl groups and thus gives rise to an inner anhydride.

Oxidation of the Condensation Product.

Freshly precipitated silver oxide in the presence of barium hydroxide was used as the oxidising agent. The silver oxide was obtained by precipitating silver nitrate with the requisite amount of barium hydroxide and washing until free from barium nitrate. It was not allowed to cake during the washing, as this materially affected the yield of acid.

Ten grams of the condensation product dissolved in 30 c.c. of water were added to 40 grams of freshly precipitated silver oxide suspended in about 400 c.c. of water. The mixture was cooled to 10°, and a solution of 10 grams of barium hydroxide in 200 c.c. of water added in portions of about 25 c.c. every five minutes. After each addition, the whole was well shaken and the temperature kept about 10°. When all the barium hydroxide had been added, the contents of the vessel were allowed to regain the room temperature. The shaking was continued at intervals of fifteen minutes for two hours. At the end of this time, the oxidation was usually complete. The silver and unchanged silver oxide were filtered off and well washed with distilled water, the filtrate and washings were mixed, and any excess of barium hydroxide precipitated by carbon dioxide. After filtering, the solution was distilled under reduced pressure until the residue became syrupy. This was dissolved in alcohol, filtered, if necessary, and the barium salt precipitated by the addition of ether. To remove any unchanged substance, the precipitate was re-dissolved in alcohol and again precipitated. The barium salt of the acid corresponding to the aldehyde, $C_8H_{14}O_3$, was thus obtained as a yellowish-white, amorphous, and very hygroscopic solid. It was dried at 100°:

0·2781 gave 0·1385 $BaSO_4$. Ba = 29·30.

$(C_8H_{13}O_4)_2Ba$ requires Ba = 28·34 per cent.

The free acid was obtained by decomposing the barium salt with the calculated amount of sulphuric acid. On filtering off the barium sulphate, boiling with a little animal charcoal, again filtering, and evaporating the filtrate under reduced pressure, the free acid was obtained as a very viscous liquid. The yield amounted to 70 per cent. The product did not crystallise even after standing for a considerable time in a vacuum over sulphuric acid. The lead, silver, calcium, and copper salts were prepared. The silver salt decomposed on drying. The lead, calcium, and copper salts were amorphous and very soluble, both in alcohol and water.

Reduction of the Acid, $C_8H_{14}O_4$, *with Hydriodic Acid.*

Ten grams of the free acid were boiled for five hours under a reflux condenser with 80 grams of hydriodic acid (b. p. 127°) and 4 grams of red phosphorus. After cooling, the liquid was diluted with twice its volume of water and extracted several times with ether. The ethereal extract was shaken with mercury to remove free iodine and the ether then removed by distillation. A thick brown oil was left behind, which still contained combined iodine. To remove this, dilute sulphuric acid was added and then zinc dust in small portions. After standing for twenty-four hours, the volatile acids were removed by distillation in steam. The distillate was neutralised with sodium hydroxide and evaporated to dryness on the water-bath. The yield of sodium salts amounted to 20—25 per cent. of the acid taken for the reduction.

5·5 Grams of the sodium salts were decomposed with sulphuric acid, and the fatty acids thus liberated were extracted with ether and dried over anhydrous sodium sulphate. The ether was removed on the water-bath and the residual fatty acid distilled. 0·85 Gram of acid passed over at 215—233°. Below 215°, a little butyric acid was obtained.* The fraction boiling at 215—233° was converted into the amide by Aschan's method (*Ber.*, 1898, **31**, 2348). After crystallising from light petroleum and then from water, the amide was obtained in glistening plates, which melted sharply at 105—106°, corresponding with the melting point of *n*-octoamide. When mixed with pure *n*-octoamide, the melting point was unchanged.

From another portion of the acid, the barium salt was prepared by neutralising with barium hydroxide. It was crystallised twice from water in order to remove barium butyrate, and was obtained in colourless plates:

0·0495 gave 0·0274 $BaSO_4$. Ba = 32·55.

$(C_8H_{15}O_2)_2Ba$ requires Ba = 32·39 per cent.

The acid obtained from the condensation product by oxidation and reduction is therefore octoic acid; hence the first stage in the condensation of aldol results in the production of a hydroxyaldehyde with the carbon atoms united in a straight chain.

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* This was due to the aldol not being completely removed from the condensation product by distillation in steam. In cases where the condensation product was not required for analysis, the steam distillation was shortened in order to lose as little as possible of the condensation product which is slightly volatile in steam.

The residue, which did not distil at 233°, was converted into the barium salt and analysed:

0·1312 gave 0·0727 $BaSO_4$. $Ba = 32·61$.

This was therefore barium octoate.

Synthesis of a-Ethylhexoic Acid.

This was carried out in the usual manner from ethylmalonic ester and butyl iodide. 1·7 Grams of sodium were dissolved in 20 c.c. of absolute alcohol and, after cooling, 14 grams of ethylmalonic ester added. 13·5 Grams of *n*-butyl iodide were now added, drop by drop, with frequent shaking. When all the butyl iodide had been run in, the mixture was heated on the water-bath for six hours, after which the alcohol was removed as completely as possible by distillation. The residue was dissolved in water, calcium chloride solution added, and the *ethylbutylmalonic ester* extracted with ether. After dehydrating the ethereal solution, the ether was removed on the water-bath and the ester distilled. Nine grams were obtained boiling at 235—245°. The ester was hydrolysed by boiling with the requisite amount of 30 per cent. aqueous potassium hydroxide. When hydrolysis was complete, the solution was extracted with ether to remove a little oily impurity, then acidified with dilute sulphuric acid, and the liberated acid extracted with ether. The ether was evaporated and the acid purified by crystallisation from water. It was obtained in colourless needles melting at 116°:

0·1035 gave 0·2191 CO_2 and 0·0769 H_2O. $C = 57·72$; $H = 8·26$.

$C_9H_{16}O_4$ requires $C = 57·44$; $H = 8·51$ per cent.

The ethylbutylmalonic acid was decomposed by heating to 165° for half an hour. The resulting *a*-ethylhexoic acid boiled at 225°. The acid was converted into the *amide* by Aschan's method (*loc. cit.*). It crystallised from water in long needles melting at 101—102°:

0·1454 gave ammonia which neutralised 10·30 c.c. $N/10$ H_2SO_4. $N = 9·7$.

$C_8H_{17}ON$ requires $N = 9·8$ per cent.

The barium salt of the acid has been previously described by Raupenstrauch (*Monatsh.*, 1887, 8, 115), who obtained the acid by the oxidation of the corresponding alcohol. Raupenstrauch states that the barium salt is amorphous. This was confirmed by preparing the barium salt of the synthetic acid which was also found to be amorphous.

a-Ethylhexoic acid is therefore easily distinguished from *n*-octoic acid by the melting point and crystalline form of its amide, and also by the fact that *n*-octoic acid gives a crystalline barium salt, whereas α-ethylhexoic acid does not.

In conclusion, I wish to express my thanks to Dr. Leathes for much kind help and advice during the course of the work.

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CLXXVI.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part X. Effect of the Configuration and Degree of Saturation of the Solvent.*

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IN the last part of this investigation (Trans., 1907, **91**, 504; see also *Ber.*, 1907, **40**, 2564) it was shown by one of us and Mr. McMillan that relatively small quantities (even 2 per cent.) of benzaldoxime and anisaldoxime affect very markedly the rotation of ethyl tartrate in which they are dissolved. Further, the *syn*-form of the oxime has a much greater effect than the *anti*-form, and it was found possible to follow the spontaneous change of the former into the latter by observing the slow alteration in rotation of the admixed active ester.

According to the theory generally accepted at present, the existence of the two forms of an oxime is to be explained by a difference in the spatial arrangement of the atoms in their molecules, and it is interesting that a difference thus represented as a comparatively insignificant detail of configuration is of such enormous importance so far as rotation is concerned. The effect of substituting *syn*-oxime for *anti*-oxime in a mixture with ethyl tartrate, containing, say, 5 per cent. of oxime, is actually greater than would be caused by replacing water by chloroform.

It seemed therefore desirable to investigate the question a little more fully by ascertaining whether the configurational difference in another pair of solvents is of equally marked effect, and, since an isomerism to some extent analogous to that postulated in the oximes is met with in maleic and fumaric acids, we have prepared the ethyl esters of these two acids and examined the rotation of ethyl tartrate dissolved in them. The experimental results were as follows.

Ethyl Tartrate in Ethyl Maleate.

The ethyl maleate was prepared from the silver salt and pure ethyl iodide. It boiled at 105–106° under 14 mm. pressure. For its density, the following data were obtained:

Temperature ...	10°	25·2°	32·5°	44·2°
Density	1·07898	1·06364	1·05637	1·0445

The ethyl tartrate used had $\alpha_{D}^{22 \cdot 1^{\circ}}$ +9·602°.

Solution I. $p = 20 \cdot 6774$.*

t°.	$\alpha_{D}^{t^{\circ}}$ (100 mm.).	Density.	$[\alpha]_{D}^{t^{\circ}}$.
12·0°	+2·912°	1·1024	+12·77°
21·4	3·006	1·0930	13·30
31·1	3·132	1·0833	13·98
41·1	3·220	1·0728	14·52
50·8	3·298	1·0623	15·01

Densities determined.

Temperature	20·3°	25·95°	33·05°	44·4°
Density	1·0943	1·0885	1·0814	1·0698

* p = grams of ethyl tartrate per 100 grams of solution.

Solution II. $p = 79 \cdot 9308$.

t°.	$\alpha_{D}^{t^{\circ}}$ (100 mm.).	Density.	$[\alpha]_{D}^{t^{\circ}}$.
13·3°	+7·630°	1·1825	+8·07°
25·2	8·694	1·1702	9·29
38·7	9·668	1·1565	10·46
46·9	10·372	1·1483	11·30
53·3	10·746	1·1417	11·78

Densities determined.

Temperature	18·15°	22·25°	30·05°	34·25°
Density	1·1774	1·1731	1·1652	1·1611

Ethyl Tartrate in Ethyl Fumarate.

The ethyl fumarate was prepared from fumaric acid, ethyl alcohol, and concentrated sulphuric acid as described by Purdie (Trans., 1881, **39**, 346.) It boiled at 98—99° under a pressure of 14 mm. Density determinations gave the following numbers:

Temperature	20·6°	30·23°	33·25°
Density	1·05189	1·04210	1·03897

Solution I. $p = 20·67835$.

$t°$.	$\alpha^{t°}_{D}$ (100 mm.).	Density.	$[\alpha]^{t°}_{D}$.
11·0°	+2·874°	1·0895	+12·76°
20·1	3·022	1·0801	13·53
31·5	3·150	1·0684	14·26
38·8	3·230	1·0606	14·73
51·9	3·354	1·0470	15·49

Densities determined.

Temperature........	15·95°	24·1°	32·3°	42·05°
Density..............	1·0844	1·0760	1·0674	1·0573

Solution II. $p = 79·982$.

$t°$.	$\alpha^{t°}_{D}$ (100 mm.).	Density.	$[\alpha]^{t°}_{D}$.
14·0°	+7·826°	1·1769	+8·31°
23·7	8·750	1·1669	9·38
29·8	9·236	1·1605	9·95
40·9	10·028	1·1491	10·91
46·3	10·436	1·1435	11·41

Densities determined.

Temperature......	19·05°	31·3°	37·0°	48·8°
Density...........	1·17178	1·15884	1·1530	1·1409

The behaviour of the two solvents may be compared by means of the following table, giving values for specific and molecular rotation at 20° obtained from the foregoing data:

Rotation of Ethyl Tartrate.

	In ethyl fumarate.			In ethyl maleate.		
	$p=0$.	$p=20·7$.	$p=79·9$.	$p=0$.	$p=20·7$.	$p=79·9$.
$[\alpha]^{20°}_{D}$	+15·60°	+13·43°	+8·98°	+15·4°	+13·27°	+8·73°
$[M]^{20°}_{D}$	32·14	27·67	18·50	31·73	27·34	17·98

The numbers reveal the fact that the difference in configuration between maleic and fumaric ester is of very little importance as regards the rotation of the ethyl tartrate dissolved in them. At both concentrations examined, the rotation of the fumaric ester solution is slightly greater than that of the maleic ester solution, but only by an amount which is not much in excess of the experimental error, and which is almost entirely negligible when compared with the corresponding difference in the case of the oximes.

In other directions also, no decided contrast in the behaviour of these esters is discernible. Only a slight difference is noticeable in the temperature coefficients for the $p=20·7$ solutions, the specific rotation of the solution in ethyl fumarate increasing on heating somewhat more rapidly than the other.

Although therefore a comparison of these two esters in regard to their solvent action reveals no striking divergence, the behaviour of both substances is of considerable interest when compared with the influence of other solvents. As dilution increases, the rotation of the dissolved ethyl tartrate rises fairly rapidly, but apparently not quite linearly, in both esters, as is shown in the diagram, so that at infinite dilution the rotations would be +15·6° in ethyl fumarate and +15·4° in ethyl maleate. The rotation of an ethyl tartrate molecule therefore, surrounded by a very large excess of molecules of maleic or fumaric ester, is practically doubled, and is thus very materially modified. In fact, of the solvents hitherto examined, these two esters are only inferior to water (Trans., 1901, **79**, 180; 1904, **85**, 1129) in increasing the rotation of ethyl tartrate.

Having thus determined the influence of these two unsaturated esters, it seemed of interest to include in the investigation the corresponding saturated compound. The result was as follows.

Ethyl Tartrate in Ethyl Succinate.

The succinic ester was prepared from the acid and ethyl alcohol by saturation with hydrogen chloride. It boiled at 104—105° under 15 mm. pressure.

Solution I. $p = 20·6721$.

t°.	$\alpha_D^{t^{\circ}}$ (100 mm.).	Density.	$[\alpha]_D^{t^{\circ}}$.
11·6°	+1·874°	1·0800	+8·39°
23·1	2·136	1·0681	9·67
31·5	2·288	1·0595	10·45
44·4	2·502	1·0460	11·57
49·9	2·600	1·0408	12·08

Densities determined.

Temperature......	19·35°	25·55°	33·95°	43·3°
Density	1·07203	1·06552	1·0567	1·0471

Solution II. $p = 79·9261$.

t°.	$\alpha_D^{t^{\circ}}$ (100 mm.).	Density.	$[\alpha]_D^{t^{\circ}}$.
13·2°	+6·524°	1·1757	+6·94°
20·8	7·348	1·1677	7·87
34·2	8·580	1·1538	9·30
42·0	9·204	1·1459	10·05
49·0	9·732	1·1385	10·69

Densities determined.

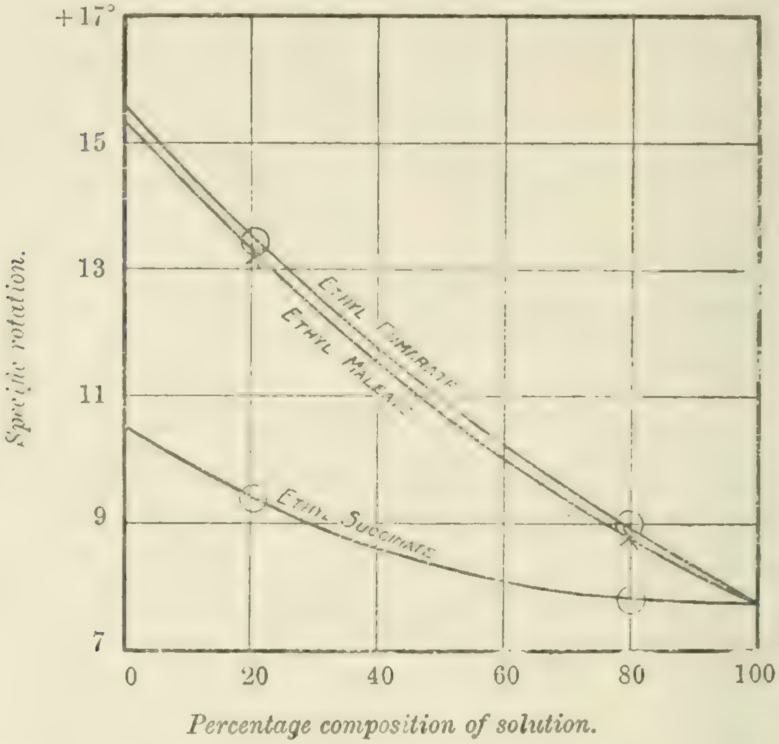
Temperature.........	20·1°	32·0°	36·75°	42·9°
Density	1·1684	1·1562	1·1515	1·1450

From these data, we obtain for the rotations at 20° the following numbers:

	$p=0$.	$p=20·67$.	$p=79·93$.
$[\alpha]_D^{20°}$	+10·5°	+9·35°	+7·80°
$[M]_D^{20°}$	21·63	19·26	16·70

The curve for the rotation of ethyl tartrate in ethyl succinate is shown in the diagram. The saturated ester also raises, to some extent, the rotation of the tartrate, but its effect in this respect is very considerably less than that of the unsaturated compounds. At infinite dilution, the respective rotations are:

Ethyl tartrate in fumaric, maleic, and succinic ester.



Solvent.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
Ethyl fumarate............	+15·6°	+32·14°
Ethyl maleate	15·4	31·73
Ethyl succinate...........	10·5	21·63

In former papers, it has been suggested that the values for specific rotation and solution-volume of an active substance in different media may be related to each other; in the case of ethyl tartrate, rotation seems to vary inversely with volume. Values for solution-volume, however, do not possess much significance, except for very dilute solutions, and in the present case, owing to the expense of the fumaric and maleic esters, we have not examined any such. Nevertheless, we have calculated the molecular solution-volumes of the ethyl tartrate in the solutions of $p = 20·67$. Unfortunately, by an oversight, the density of the succinic ester with which the observations recorded above were made was not determined. A fresh specimen gave these numbers:

Ethyl Succinate.

Temperature	19°	24·8°	23·04°	31·75°
Density	1·0116	1·03513	1·03228	1·02841

A solution of ethyl tartrate in this ester, of $p = 20·6699$, gave $d 20°/4°$: 1·07102.

Molecular Solution-volume of Ethyl Tartrate.

Solvent.	p.	d.	δ.	M.S.V.$^{20°}$.	$[\alpha]_D^{20°}$.
Ethyl fumarate......	20·67835	1·08021	1·0525	171·44 c.c.	+13·13°
Ethyl maleate	20·6774	1·09461	1·06892	170·74 ,,	13·27
Ethyl succinate......	20·6699	1·07102	1·01050	170·72 ,,	9·35

The molecular volume of ethyl tartrate is 170·91, so that there appears to be some slight expansion in the fumaric ester solution, and a trifling contraction in the solutions in maleic and succinic ester, but the changes are only very small and scarcely sufficient from which to draw any definite conclusions. So far as they go, the results are not in accordance with the suggestion mentioned above, since with practically the same solution-volume in ethyl maleate and ethyl succinate the rotations are distinctly different, whilst with slightly different solution-volume in ethyl fumarate and ethyl maleate the rotations are very nearly equal.

The idea that solution-volume and rotation are causally related does not necessarily involve any assumption as to the mechanism of solution, but is certainly simplest if solute and solvent be regarded as entirely independent, a view which has been tacitly adopted hitherto in the present investigation. At its inception, the modern theory of solution included this assumption, and for fairly satisfactory reasons. Gradually, however, opinion has altered to such an extent that at the last meeting of the British Association, "Prof. Abegg reminded Prof. Armstrong that combination between solute and solvent is admitted by everyone."* It is perhaps to be regretted that such grounds for this admission as can be advanced are not so convincing as the statement itself is concise, and we incline to the belief that the question may at present be regarded as absolutely an open one, although Abegg disposes of the matter in the following simple manner (*Zeitsch. anorg. Chem.*, 1904, **39**, 353): "Ferner gehört in diese Gruppe das grosse

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* Report in *Nature*, 1907, **76**, 460.

Gebiet der Lösungen die nach unsern Ausführungen zum grossen Teil ebenfalls als lose Verbindungen von gelöstem Stoff und Lösungsmittel aufzufassen sind. . . . Eine chemische Lösung in unserm Sinne liegt in allen Fällen vor, wo beim Vermischen der Komponenten Wärmetönungen, Volumänderungen, optische Änderungen eintreten, kurz wo die Mischung nicht absolut additiv die Eigenschaften ihrer Bestandteile repräsentiert."

Now the suggestion that rotation changes in solution are due to the formation of loose and easily dissociated molecular compounds is a perfectly legitimate one, but it must be consistently worked out. It by no means follows, for instance, that because the volume of a mixture was exactly the sum of the volumes of its constituents therefore no complex-formation had occurred. Abegg's next remark is sufficient to destroy any faith which might be inspired by the confidence of the statement just quoted. "Als physikalische Mischungen ohne chemische Bindung sind auch die idealen verdünnten Lösungen aufzufassen, die ja durch das Fehlen der obigen Erscheinungen definiert sind. Bei ihnen ist die chemische Kraft zwischen Lösungsmittel und gelöstem Stoff . . . . so gering geworden, dass der Zerfall der bei höhern Konzentrationen vorhandenen Lösungsverbindungen praktisch vollkommen ist" (*loc. cit.*, 354). This statement suffers from two most serious defects. Firstly, it involves the very difficult question as to the point at which concentrated solutions end and dilute solutions begin. According to Abegg, they differ in character. Therefore it would be necessary to ascribe change of rotation in concentrated solution to combination, and in dilute solution to some other cause not specified. Secondly, the statement is unfortunately a flat contradiction of the law of mass action. If an active substance, A, combine with solvent, S, according to the equation:

$$A + nS \rightleftharpoons ASn,$$

then obviously the greater the proportion of solvent present the greater will be the percentage number of molecules which combine with solvent molecules, and the greater should be the alteration in the *specific rotation* of the active compound. If C, C_1, and C_2 be the concentrations of A, B, and AB_n respectively, then

$$KC_2 = CC_1{}^n,$$

and, since most of the quantities occurring in this equation cannot meanwhile be determined for solutions such as those dealt with here, it is impossible to compare the rate of formation of complex molecules with the rate of change of rotation. When it is borne in mind that this is the simplest statement of the matter, and that perhaps other equilibria must be taken into account before a satisfactory agreement between theory and experiment could be hoped for, it seems clear that the possibility of attacking the problem from this side is somewhat remote.

Nevertheless, we think that the data recorded in this paper may be discussed in regard to combination between solute and solvent, since it is possible to institute what is probably a legitimate comparison between the solutions which we have examined, on the one hand, and actual chemical compounds on the other.

Thus it is an interesting fact that an unsaturated radicle in an active molecule has a much greater effect on the rotation of the compound than the corresponding saturated radicle.

Thus Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 569) found these data:

Diamyl fumarate	$[M]_D$	+15·17°
Diamyl succinate	,,	9·70

Rupe (*Annalen*, 1903, **327**, 157) gives values proving a similar behaviour for various menthyl esters. For instance:

Menthyl crotonate	$[M]_D^{20°}$	−203·1°
Menthyl butyrate	,,	164·7
Menthyl benzoate	$[\alpha]_D^{20°}$	−83·53°
Menthyl hexahydrobenzoate.........	,,	59·11

Haller and Muller (*Compt. rend.*, 1899, **128**, 1370) found:

Benzylidenecamphor	$[\alpha]_D$	+421·25°
Benzylcamphor........................	,,	181·82

In each case, the asymmetry of the molecule is increased by the conversion of a single into a double bond, and, although it would be rash to assert that this behaviour will occur in all cases, it seems, so far as we know at present, to be general.*

If, then, combination occur between ethyl tartrate and ethyl fumarate, on the one hand, and between ethyl tartrate and ethyl succinate, on the other, it might be expected that the former solution should have the higher rotation, and this is indeed the case. At infinite dilution, we find:

Ethyl tartrate in ethyl fumarate.........	$[M]_D^{20°}$	+32·14°
Ethyl tartrate in ethyl succinate.........	,,	21·63

The difference of 10·51° is thus considerably greater than that found by Walden (5·47°) on comparing the rotations of actual compounds.† The rotation difference is thus quite significant enough to justify the view that it may be due to combination of active substance and solvent.

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* Nevertheless, some reservation is necessary, since Rupe's experiments show that the position of the double bond in the molecule is an important factor in determining the rotation. At a distance from the point of attachment of the radicle to the rest of the molecule it has very little effect.

† The amyl alcohol used by Walden was not pure and therefore the difference, 5·47°, is too small.

There is, however, another side to this argument, for Walden has found that the *l*-amyl esters of fumaric and maleic acids differ considerably:

Di-*l*-amyl fumarate	$[M]_D$	+15·17°
Di-*l*-amyl maleate	,,	11·82

Consequently, it might be expected that if ethyl fumarate and ethyl maleate combine with ethyl tartrate in solution, there should be a much more distinct difference in rotation than actually exists.

It is thus evident that the argument on one side of this question is opposed by one equally or almost equally strong on the other, but the importance of the problem will, we hope, justify a discussion from which, for our own part, we do not venture, meanwhile, to draw any definite conclusion.

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CLXXVII.—*Two Volumetric Methods for the Determination of Chromium.*

By Arnold William Gregory, B.Sc. (Lond.), and James McCallum.

I.

When ammonium persulphate is added to a solution of a chromium salt in the presence of silver nitrate and nitric acid, the chromium is oxidised to chromic acid.

Upon this reaction, H. E. Walters (*J. Amer. Chem. Soc.*, 1905, **27**, 1550) bases a method for the determination of chromium in steel. In this case, the manganese present is converted into permanganic acid, and the chromium into chromic acid. These two are estimated together by means of ferrous sulphate solution, and the permanganic acid alone by means of sodium arsenite.

This method, although capable of giving good results, has the objection that the chromium is determined by difference, and an appreciable error may thus be introduced where only small quantities of chromium are present.

Kleine (*Stahl und Eisen*, 1905, **25**, 1305; 1906, **26**, 396) removes manganese by first treating a solution of steel in nitric acid with persulphate alone. The manganese is thus converted into manganese dioxide, and may be filtered off. He then removes iron by extracting the solution with ether, and estimates chromium in the aqueous solution by the persulphate-silver nitrate method.

This process is long, and the removal of the iron appears to us to be a superfluous operation.

The following process has been found to give trustworthy results, and it requires a minimum of time for its performance.

If manganese is absent, the solution is acidified with nitric acid and 20 c.c. of a 1 per cent. solution of silver nitrate added. To this mixture, about 10 grams of ammonium persulphate are added, and the solution boiled for five minutes. The chromium is thus converted into chromic acid, and the excess of the persulphate is decomposed. In order to make quite certain that no persulphate exists in this solution, a few c.c. of a dilute solution of manganese sulphate are now added. If persulphate is present, permanganic acid will be formed, and this may be decomposed by adding a dilute solution of hydrogen peroxide, drop by drop, until the permanganate colour just disappears. (A large excess of hydrogen peroxide must not be used, or reduction of the chromate may occur.) The solution is once more brought to the boiling point, to expel oxygen, and then cooled and diluted. An excess of standard ferrous sulphate solution is now added, and the excess titrated back with standard dichromate solution. From the data so obtained, the amount of chromium may be calculated.

In the determination of chromium in iron and steel containing manganese, the process is as follows. Two grams of the iron or steel are dissolved in as little nitric acid as possible, and silver nitrate and persulphate added in the usual way. The solution is boiled for a few minutes, and a quantity of ammonium chloride solution is added, such that nearly all the silver is precipitated as chloride. On boiling, the permanganic acid is partly converted into manganese chloride and partly decomposed with the formation of hydrated oxide of manganese. The solution is now diluted to a definite volume, and filtered through an asbestos filter. A quantity of the filtrate, equal to one-half the original volume of the solution, is taken and treated in the same manner as described in the preceding process. The fact that silver nitrate is present in excess during the whole of the process, precludes the possibility of free chlorine being present in the solution.

In making up the solution to a definite volume, no account is taken of the volume of the precipitate, but, as the percentage of chromium present in iron and steel is comparatively low, no appreciable error is introduced on this account.

By working with sufficiently dilute standard solutions, the merest traces of chromium may be accurately determined by this method.

Instead of using a solution of ammonium chloride, a dilute solution of hydrogen peroxide may be employed to reduce the permanganic acid.

We attempted to estimate manganese and chromium in steel simultaneously by converting into permanganic and chromic acids respectively, and then titrating the former with hydrogen peroxide until the pink colour disappeared, whereupon the chromic acid remaining was titrated with ferrous sulphate solution.

The results obtained were, however, untrustworthy, since oxidation of the chromic acid to perchromic acid began before all the permanganic acid was reduced by the hydrogen peroxide.

EXPERIMENTAL.

A solution was made of two grams of chromium-free steel in nitric acid, and to this, 10 c.c. of a solution of chromium sulphate were added. (1 c.c. $=0·003$ gram of chromium.)

After oxidation, 28 c.c. of ferrous sulphate were added. On titrating back with potassium dichromate solution (1 c.c. $=0·003$ gram of chromium), 1·2 c.c. were required. Ten c.c. of the potassium dichromate solution were equivalent to 24·8 c.c. ferrous sulphate solution:

Found, $Cr=0·0302$ gram.
Used, $Cr=0·0300$ gram.

Varying amounts of chromium were taken, and equally good results were obtained.

II.

Oxidation by Means of Sodium Bismuthate.

When sodium bismuthate is added to a solution of a steel containing chromium, the chromium is oxidised to chromate. This reaction takes place instantly if the solution is boiled. At the same time, the manganese is converted into permanganic acid (Ibbotson and Brearley, *Chem. News*, 1901, **84**, 247, 269). On boiling, the manganese is precipitated as manganese dioxide.

We have obtained excellent results by proceeding in the following manner. Two grams of the iron or steel are dissolved in nitric acid, and about 3 grams of sodium bismuthate added in small quantities. The solution is then boiled until all the manganese is precipitated as dioxide. A small quantity of very dilute hydrochloric acid is now added, whereupon the manganese dioxide is dissolved. Excess of silver nitrate is then added, and the solution boiled, when silver chloride is precipitated. The solution is filtered through an asbestos filter, and titrated in the usual way.

EXPERIMENTAL.

A solution was made of 2 grams of chromium-free steel in nitric acid, and to this, 20 c.c. of a solution of chromium sulphate were added. (1 c.c. = 0·003 gram of chromium.)

After oxidation, 51 c.c. of ferrous sulphate solution were added.

The excess of ferrous sulphate required 0·5 c.c. of potassium dichromate solution. (1 c.c. = 0·003 gram of chromium):

Found, Cr = 0·0602 gram.

Used, Cr = 0·0600 gram.

Equally good results were obtained with smaller quantities of chromium.

APPLEBY IRON WORKS,
FRODINGHAM.

CLXXVIII.—*The Atomic Weight of Tellurium.*

By HERBERT BRERETON BAKER and ALEXANDER HUTCHEON BENNETT.

THE exception to Mendeléeff's periodic classification presented by this element has led to an enormous amount of work being done on the subject during recent years. Since the atomic weight is about 0·7 above that of iodine, tellurium appears to fall into a position remote from its congeners, sulphur and selenium. Many hypotheses have been offered to explain the reason of this; Brauner, who worked at the problem for six years (Trans., 1889, **55**, 382), believed that tellurium is not a homogeneous substance, but that "it is a mixture of two elements which cannot be separated by ordinary chemical means" (*Watts Dict.*, **4**, 652, *private communication*). Scott (Proc., 1902, **18**, 112) from a consideration of the differences of the atomic weights of the elements in this group from those of their neighbours came to the conclusion that the atomic weight of tellurium should be above that of iodine. Since 1889, no less than seventeen papers have been published on this subject; in fact, no element has had its atomic weight more rigidly scrutinised than tellurium during this period.

Our own work began in 1894, and has been carried on continuously for the last thirteen years. It originated in the discovery by one of us (Baker, *Phil. Trans.*, 1888, **179**, 571) that tellurium is one of the few elements which will burn in dried oxygen. It was thought that, since the combustion of carbon disulphide containing elements which do not so burn, is unaffected by the presence of moisture, tellurium might prove to be a compound. The element has been obtained from several sources, namely, from Bohemian tellurium, from West Australian gold ores, from South American copper ores, and lastly, a specimen prepared by Prof. Divers from Japanese sulphur deposits was used. The purification of the element was, in addition to special treatment described later, conducted as follows. The substance was dissolved in *aqua regia*, evaporated several times with hydrochloric acid, diluted with water containing a little sulphuric acid, filtered, and saturated with sulphur dioxide. In this way, most of the gold, silver, bismuth, lead, thallium, and selenium was removed. After washing and drying, the finely-divided element was fused with sodium and potassium cyanides in a current of coal gas. This operation was most conveniently carried on in a porcelain basin covered by another basin, a clay pipe carrying coal gas being inserted in the space formed by the two lips of the basins. The mass on cooling was introduced into a large flask provided with a reverse filter, a tube leading in coal gas, and a tap funnel. Previously boiled water was added, and the red liquid drawn through the filter into a large filtering bottle. By drawing a current of air through the solution the tellurium was precipitated in long, needle-shaped crystals. After very thoroughly washing, the tellurium was converted into telluric acid by the action of nitric and chromic acids. After many recrystallisations, the acid was dried and heated, the dioxide produced was dissolved in hydrochloric acid, and the solution reduced either by sulphurous acid or by hydrazine hydrate. The element was finally distilled in the purest hydrogen obtainable, prepared by the electrolysis of very pure barium hydroxide solution.

Attempts to Separate Tellurium into Two Elements.

I.

On the hypothesis that another element is present of higher atomic weight in the same group, a separation might be expected by the fractional crystallisation of the acid. Since sulphuric acid, selenic acid, and telluric acid form a series of increasing insolubility in water, one might expect that the acid formed by the unknown element would be obtained in the first fractions of the recrystallised telluric acid.

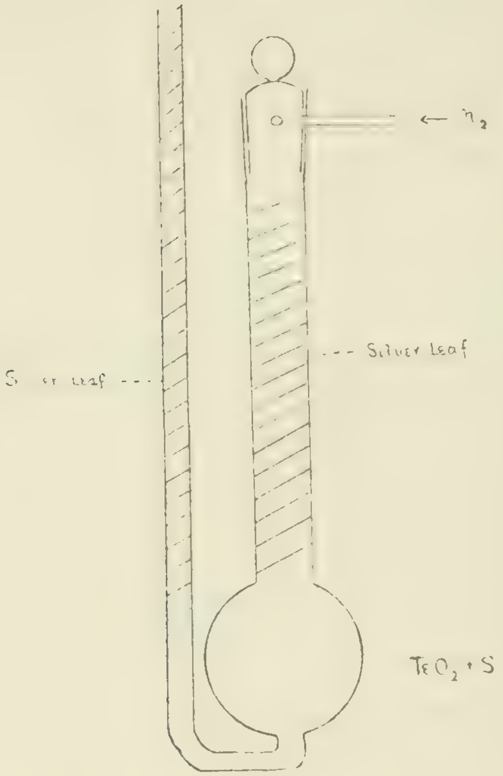
The telluric acid was obtained by two distinct methods. In the first method (Berzelius), the element was oxidised by nitric acid to which a small quantity of hydrochloric acid was added. The oxide was fused with sodium nitrate, giving a mixture of the normal and tetra-tellurates. The latter is not only insoluble in water and alkalis, but is not decomposed by long boiling with *aqua regia*. The solution of the tellurate was precipitated by barium hydroxide, which had been recrystallised eight times, and the barium tellurate decomposed by boiling with defect of dilute sulphuric acid. The solution of telluric acid was fractionally crystallised.

The second preparation of the acid, which, if the tellurium were a mixture, would probably give different results, was carried out by the process recommended by Staudemaier (*Zeitsch. anorg. Chem.*, 1895, **10**, 189). The element was dissolved in nitric acid, and to the strongly acid solution the equivalent quantity of chromium trioxide was added. After boiling for an hour, the telluric acid crystallised out on standing. The crystals were drained on an asbestos filter, and by washing with alcohol they were obtained nearly free from chromium nitrate. By recrystallising four times, the acid was obtained in beautiful crystals, free, as far as could be detected by chemical testing, from all impurities. The acid contains two molecules of water of crystallisation.

A large number of determinations of the equivalent were made by heating a weighed quantity of the acid, and weighing the residual dioxide. In spite of all precautions, constant results could not be obtained, the variation in twenty-six determinations being from 126·8 to 128·2. There is no doubt that in this, as in several other cases of salts containing water of crystallisation, the water is not a truly constant amount. Two further methods were attempted in order to surmount this difficulty.

The first was to obtain the ratio of $TeO_2 : O$ in the acid. The weighed acid was contained in a tube of hard glass connected by a ground joint with a small condenser to a Töpler pump. On heating the acid in the evacuated tube, the oxygen was collected in the pump, the water being condensed on the way, and the gas afterwards measured in a carefully calibrated gas pipette. The results were unsatisfactory; however carefully the heating was begun, a little spurting of the acid in the vacuum could not be prevented, and the method was abandoned. The second attempt to determine the same ratio was to heat the acid in a hard glass tube in a current of nitrogen, the oxygen being absorbed in a second tube containing red-hot copper. The results were, however, not constant, and another method was employed, which, as far as we can find, has only been used once before, in a single determination by Berzelius of the equivalent of arsenic. The method is a very elegant one, which is applicable to many elements which lie on the border line between the metals and the non-metals. It consists in weighing a quantity of the oxide in a special tube (Fig. 1), adding highly purified sulphur, and packing the two ends of the tube with pure silver leaf. The tube is weighed again. It is then filled with dried nitrogen, and the mixture heated with the smallest flame of an Argand burner. The reaction between the sulphur and the oxide begins at 130°, and proceeds slowly, being complete in about an hour. The silver most effectively stops any loss of sulphur vapour, and the loss in weight of the tube is due to sulphur dioxide only, from which the percentage of oxygen in the oxide of tellurium is readily calculated. The results of the experiments are given below, the weights being calculated to vacuum standard, and assuming O = 16, S = 32·06.

FIG. 1.



Fractional Crystallisation of Telluric Acid Prepared from Barium Tellurate (26 grams of acid used).

Fraction.	Weight of tellurium dioxide taken.	Loss in weight (sulphur dioxide).	Percentage of oxygen in TeO_2.
I.	1·51509	0·60838	20·055
II.	1·09875	0·44074	20·034
III.	1·02150	0·40993	20·046
IV.	0·90835	0·36472	20·053
V.	1·00702	0·40451	20·062
VI.	1·01515	0·40733	20·044

Fractional Crystallisation of Telluric Acid Prepared by Oxidising the Element with Nitric and Chromic Acids (167 grams of acid used).

Fraction.	Weight of tellurium dioxide used.	Loss in weight (sulphur dioxide).	Percentage of oxygen in TeO_2.
I.	1·56837	0·62938	20·046
II.	1·07852	0·43257	20·035
III.	1·72627	0·69296	20·052
IV.	2·09253	0·83927	20·032
V.	0·83335	0·33465	20·059
VI.	1·15372	0·46284	20·041
VII.	1·68618	0·67661	20·045
VIII.	0·90835	0·36472	20·053

The results afford no evidence of any separation brought about by the fractional crystallisation of telluric acid.

Sir William Crookes was kind enough to examine spectroscopically tellurium from the first and last fractions of the crystallisation of telluric acid, series II. The beautiful spectra which he obtained showed the complete identity of the element from the two fractions.

II.

A second series of experiments on the possible decomposition of tellurium was based on the progressive solubility of the barium salts of the acids, as one descends the series. Barium sulphate is one of the most insoluble salts known, barium selenate less so, whilst barium tellurate is appreciably soluble in water. If therefore tellurium contains an element of higher atomic weight in the same series, the barium salt of its acid ought to be fairly soluble. In order to test this, a quantity of the purest acid used in the last experiments was neutralised with very pure barium hydroxide in concentrated solution, a slight excess of the base was then added, and carbon dioxide passed into the solution to precipitate any uncombined barium hydroxide. The mixture was evaporated to a small bulk on the water-bath and filtered. The precipitate was then boiled with 3 litres of distilled water, and the hot liquid filtered off. The solution was evaporated, and the crystallised barium salt thus obtained was converted into the acid by dilute sulphuric acid. This was heated to give the dioxide, and the undissolved barium tellurate was treated in the same way. The atomic weight of the element found in the two specimens of the oxide showed no difference, the numbers being:

From soluble barium tellurate,	127·60
„ insoluble „ „	127·61.

III.

Fractional Distillation.

Experiments were made first on the element, which was fractionally distilled (1) in a vacuum, (2) in the very pure hydrogen obtained by the electrolysis of barium hydroxide solution. The different fractions gave the same atomic weights. The spectra of these fractions were photographed, and showed no difference, the large spectroscope bequeathed to Oxford University by the late Duke of Marlborough being used for this purpose. Since, however, many known tellurides are volatile without decomposition, it was thought that compounds with negative elements or groups might be tried with advantage. The first substance chosen was ethyl telluride, a considerable quantity of this substance being prepared by Wöhler's method. These experiments had to be abandoned, however, owing to the unpleasant physiological effects of the vapour, and the more than repulsive odour which workers with it contract. As our ordinary work during the daytime brought us into contact with many other persons, it was found necessary to choose some less offensive compound. It may be mentioned that clothes worn during the preparation of the substance were left in the open air for a month, and, in spite of their exposure to rain and wind, it was necessary to burn them at the end of this period.

The next substance submitted to fractional distillation was the tetrachloride. The purified element was treated by purified chlorine obtained from pyrolusite and hydrochloric acid. The operation was carried on in a glass tube, to the end of which was sealed a series of seven bulbs in which the fractions were collected. Since chlorine obtained by the method used contains traces of oxygen, it was supposed that, as in the case of antimony chloride, some oxychloride of tellurium might be found. Before the distillation, therefore, a current of hydrogen chloride was passed over the heated chloride, and this was followed by a current of nitrogen. The most rigid precautions were taken to avoid the access of moisture. The tetrachloride thus prepared was almost pure white. The analysis of four fractions was made by dissolving the contents of the bulbs in tartaric acid solution, and adding the silver nitrate from a weighed quantity of silver prepared by Stas's bisulphite method. The precipitation was completed by the addition of $N/100$ silver nitrate from a weight burette. The atomic weights were:

Fraction	I.	127·58.
„	III.	127·60.
„	V.	127·64.
„	VII.	127·62.

It was thought that in spite of the precautions, oxychloride might still have been formed and not removed, so that a series of fractionations of the tetrabromide was performed, since if very pure bromine is used there is no difficulty in conducting the preparation and distillation in complete absence of oxygen. The bromine used was obtained by the method described by Stas, the purified bromine being distilled from purified zinc oxide and potassium bromide. After the preparation of the bromide, it was found that the substance could not be distilled without dissociation, even if the temperature is kept at the lowest possible point. If the temperature is raised much above the volatilisation point, the vapour breaks up with the manifestation of a multitude of glowing sparks which completely fill the tube. Distillation in a vacuum was found also to produce dissociation, dibromide being visible in each of the bulbs in which the fractions were collected. In order to get rid of this, a current of nitrogen laden with bromine vapour was led through the bulbs, and a current of nitrogen alone was passed for some hours until the issuing gas gave no reaction with potassium iodide and starch. On analysing the fractions, however, the amount of bromine found was much too high, probably owing to a combination or absorption of bromine by the bromide. It was therefore thought to be advisable to choose another substance free from such complications.

Fractional Distillation of the Dioxide.—Considerable difficulty was experienced in distilling this substance. It volatilises only at a red heat, and at this temperature it was found to attack porcelain and platinum. Success was ultimately attained by distillation in a quartz tube heated by a small electric resistance furnace. The oxide was obtained from recrystallised telluric acid. Even quartz is so much attacked by the heated dioxide that it was not found possible to obtain a determination from the residue. Hence the comparison was made between the distilled dioxide and a sample of the original dioxide used in the experiment. The determinations were made by the sulphur method described above.

First distilled oxide contained 20·050 per cent. of oxygen.
Original „ „ 20·052 „ „

Hence no difference is caused by this treatment.

IV.

Conversion into Tellurium Hydride.

There is a progressive change in stability of the hydrides of this group as the atomic weight increases, the dissociation of hydrogen sulphide beginning about 500°, that of hydrogen selenide about 270°, whilst hydrogen telluride dissociates at the ordinary temperature. If therefore there is an element in the same group associated with tellurium, it would be expected that its hydride would scarcely be formed at any but very low temperatures. Hence tellurium prepared from the hydride should be free from any element in the same group which had a higher atomic weight.

In the earlier stages of the research, a large amount of work was done in order to find a method of obtaining the hydride of tellurium in quantity. Direct synthesis, the decomposition of the tellurides of potassium, and magnesium gave very small yields, but the action of water on aluminium telluride gave rather better results, the yield from 20 grams of tellurium being from 0·1 to 0·3 gram. Some 10 grams of the purified element were accumulated by this tedious process in six months, but by the carelessness of a workman passing through the laboratory the whole of it was lost. In three months more, 6 grams of tellurium were obtained; it was converted into telluric acid by chromic acid, and this after recrystallisation was decomposed into the dioxide.

The percentage of the oxygen in this oxide was found in two experiments to be 20·062 and 20·058, thus showing no difference from the original substance. Further experiments on a larger scale were rendered possible by the discovery by Ernyei of an electrolytic method for the production of tellurium hydride. A lump of purified tellurium was made the cathode in the electrolysis of dilute sulphuric acid. The gas passed through a horizontal tube which was heated to about 150° in order to decompose the hydride formed. The deposited tellurium was purified from possible contamination of sulphur by fusion with sodium and potassium cyanides, and it was finally distilled in a current of hydrogen prepared by the electrolysis of barium hydroxide. By similarly treating the tellurium which was left in the electrolytic vessel, a comparison could be made directly of the element which had, and that which had not, been converted into the hydride.*

For these determinations another method was used for the determination of the equivalent. A quantity of the element was powdered in an agate mortar and weighed in the apparatus (Fig. 2), which was made of Jena glass. This was then filled with dried nitrogen, and highly purified bromine (see p. 1855) poured through a drawn-out funnel into the upper bulb. The bromine was added in very small quantities at a time to the powdered tellurium in the lower bulb, and the apparatus allowed to stand, well-stoppered, for twelve hours. It was then heated to 50° in a specially constructed air-bath, a current of dried nitrogen being passed through until the issuing gas gave no reaction with potassium iodide, showing that the excess of bromine had been expelled. The nitrogen was displaced by a current of dried air and the apparatus was transferred to the balance case. The method has the advantage of simplicity, and avoids any transference from one vessel to another. The Jena glass proved very resistant to bromine, an apparatus which was used for six determinations showing a loss in weight of less than 0·0001 gram for the whole period. A similar tube was used as a counterpoise, and, since the tetrabromide is somewhat hygroscopic, the tubes were fitted with well-ground stoppers. The apparatus was made of as thin glass as could be procured; when empty, it weighed 12 grams. It was shown that the tetrabromide is unaffected by dried air.

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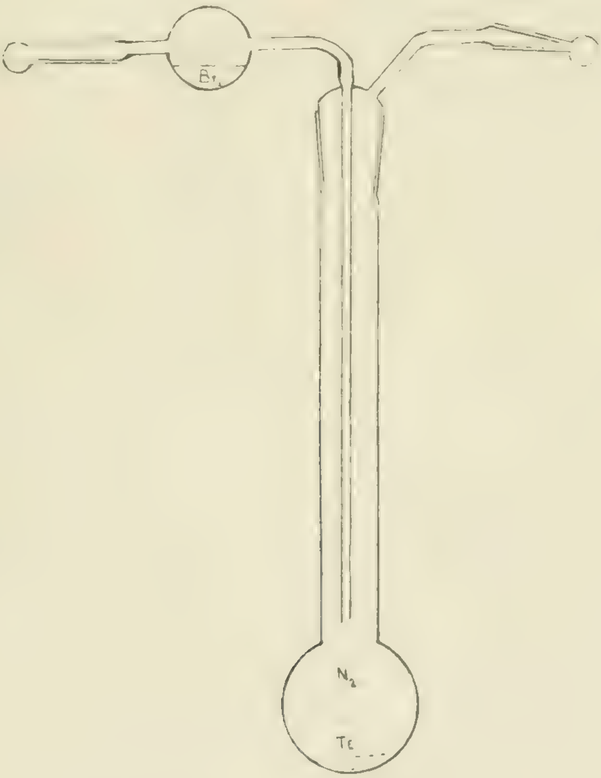
* It is not generally known that tellurium hydride is poisonous. All the time we were working with this gas, we both suffered from severe headaches, although as little as possible of the gas was allowed to escape into the air. On one occasion, one of us inhaled, by accident, a bubble of the gas. It caused a very severe attack of vertigo, which lasted for three days, and was accompanied by a low temperature, 95·2—95·8° F.

FIG. 2.



The results of the determinations are given below:

Tellurium Prepared from the Hydride.

No.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0·61273	2·14933	28·508
2.	0·56866	1·99354	28·525
3.	0·59884	2·09951	28·523
4.	0·57894	2·03040	28·514
5.	0·54743	1·91899	28·527
6.	0·33859	1·18732	28·517
7.	0·56866	1·99354	28·526
8.	0·47643	1·67025	28·525
9.	0·56622	1·98597	28·511
		Mean............	28·519

The determinations made with the tellurium which remained after the hydride had passed off:

No.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0·44271	1·55205	28·524
2.	0·41671	1·46177	28·508
3.	0·50611	1·77489	28·515
		Mean............	28·515

In the case of the tellurium in determinations 7, 8, and 9, the tellurium hydride was passed through a tube heated by a water-jacket to 35°, and only the tellurium hydride which survived this treatment was taken for the source of the tellurium. No difference was apparent in the tellurium obtained in this way.

In order to compare the results of this method with the method of heating the dioxide with sulphur, a quantity of the tellurium from the hydride was converted into the oxide by heating with purified nitric acid. The residue was heated to about 450° for several days in order to decompose the last traces of the basic nitrate. Attempts to quicken this operation resulted in failure. When, for instance, the oxide was moistened with ammonia and heated, it acquired a grey tint which was not lost by long-continued heating in air.

Analysis of Tellurium Dioxide Prepared from Tellurium Hydride.

No.	Weight of dioxide.	Loss in weight (sulphur dioxide).	Percentage of oxygen in TeO_2.
1.	1·02217	0·41050	20·064
2.	0·80697	0·32322	20·051
3.	1·32003	0·52992	20·053
4.	1·05207	0·42221	20·047
5.	1·37043	0·54969	20·032
6.	0·95944	0·38511	20·048
		Mean............	20·049

The agreement between the results obtained by the two methods is satisfactory. By the tetrabromide method, the atomic weight (Br = 79·96) is 127·601, whilst by the method of reduction by means of sulphur the atomic weight is 127·609.

Attempt to Separate Tellurium by Fractional Electrolysis.

These experiments were made at the suggestion of Prof. Abegg and Mr. F. W. Watkin.

About 20 grams of the tellurium which had been converted into the hydride were converted into the tetrabromide, and this was dissolved in the smallest possible quantity of hydrobromic acid. A carbon rod, which had been heated to redness in chlorine and well washed, was placed in a small porous pot and used as the anode. This rested on a glass triangle in a large platinum dish, which was made the cathode. A current of 0·1 ampere was used, and each fraction was the result of about 12 hours' electrolysis. The deposit on the platinum dish was dissolved by hot concentrated sulphuric acid. The solution was precipitated by sulphurous acid, washed, dried, and distilled in hydrogen.

In the first series of experiments by this method, a high atomic weight (129·02) was obtained from the first fraction. On testing the tetrabromide, however, it was found to contain a trace of platinum. In subsequent determinations, each fraction was fused with potassium cyanide, the solution of potassium telluride filtered off, decomposed by water, and the resulting tellurium then distilled in hydrogen. The results were:

Series II; 25 grams of tellurium tetrabromide used.

Fraction.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0·37382	1·31081	28·519
2.	0·31895	1·11868	28·512
3.	0·48931	1·71554	28·522
4.	0·47156	1·65404	28·510

Series III; 160 grams of tellurium tetrachloride used.

1 (1).	0·40748	1·42867	28·523
1 (2).	0·62013	2·17449	28·518

Through an unfortunate accident, this fractionation could not be continued, but the experiments on the first fraction indicate that little was to be hoped for in the way of separation.

Attempted Separation by the Decomposition of the Chloride by Water.

It seemed possible that closely-allied elements might be separated to some extent by this method. To find out if this were so, the case of mixed antimony and bismuth chlorides was given to the students working in the laboratory at a course of inorganic problems. Somewhat to our astonishment, Mr. Walling, of Magdalen College, succeeded, by cautious addition of water to the mixed chlorides, in obtaining a complete separation of antimony from bismuth. The method was then used with tellurium chloride. It was thought that if the chlorides of two elements were present, the precipitation as oxychloride of the one with lower atomic weight would, as in the case of antimony and bismuth, take place first.

About 35 grams of the tetrachloride were dissolved in the minimum quantity of dilute hydrochloric acid and 50 c.c. of water were added. The slight cloudiness which was first formed developed into a precipitate in the course of twelve hours. This was filtered off, reduced by sulphur dioxide, and distilled in hydrogen. The process was repeated and four fractions were obtained, of which the second was by far the largest:

Fraction.	Weight of tellurium.	Weight of tellurium tetrabromide.	Percentage of tellurium.
1.	0·37382	1·31081	28·519
2.	0·50822	1·78207	28·518
3. (very small)	0·12928	0·45354	28·505
4.	0·42926	1·50540	28·515

For the sake of comparison, we add two determinations made with tellurium from the sulphur deposits in Japan. This was kindly lent to us by Prof. E. Divers, who had himself purified it very carefully. It was only thought necessary to redistil it in hydrogen:

Japanese Tellurium.

No.	Weight of tellurium.	Weight of tellurium tetrabromide.	Percentage of tellurium.
1.	0·80348	2·81715	28·511
2.	0·95309	3·34193	28·512

The balance used throughout this research was one of Oertling's No. 5, made some twenty-five years ago. The weights were standardised among themselves, and the figures given in the paper are the weights calculated to vacuum standard. The mean of the twenty-five determinations of the oxygen in tellurium dioxide by the sulphur method gives the percentage as 20·048, the atomic weight of tellurium calculated from this (O = 16) is 127·609.

The mean of the eighteen determinations of the tellurium in the tetrabromide is 28·518, from which, assuming Br = 79·96, the atomic weight of tellurium is 127·601. Since the latter method is a priori the better one, we incline to think that 127·60 is the nearer to the true constant.

General Conclusions.—No difference could be distinguished in the atomic weight of tellurium when:

1. Telluric acid, obtained by two distinct methods, was fractionally crystallised;
2. Barium tellurate was dissolved in water;
3. Tellurium was fractionally distilled;
4. Tellurium tetrachloride was fractionally distilled;
5. Tellurium dioxide was fractionally distilled;
6. Tellurium was converted into the hydride, and fractionally decomposed;
7. Tellurium tetrabromide and tetrachloride were submitted to fractional electrolysis;
8. Tellurium tetrachloride was fractionally precipitated by water.

The atomic weight of tellurium is 127·60.

Highly purified tellurium does not burn in dried oxygen.

The work was carried on for eight years in the laboratory at Dulwich College, S.E., for one year in a private laboratory, and for the last four years in the new research laboratory at Christ Church.

We wish, in conclusion, to express our thanks to Sir William Crookes for his examination of the spectrum of the element, to Prof. Divers for the loan of Japanese tellurium, and to the Committee of the Research Fund of the Chemical Society for a grant for the purchase of material.

Christ Church,
Oxford.

CLXXIX.—*Gaseous Nitrogen Trioxide.*

By Herbert Brereton Baker, M.A., D.Sc., F.R.S., and Muriel Baker.

Nitrogen trioxide has been shown to exist (Ramsay and Cundall, Trans., 1885, **47**, 187; Ramsay, Trans., 1890, **57**, 590) in the green liquid obtained by the condensation of the gas evolved by the action of nitric acid on arsenic trioxide. It was found that on allowing the liquid to evaporate, almost complete dissociation took place, and the gas consisted almost entirely of nitrogen peroxide and nitric oxide. The discovery by one of us that traces of moisture were necessary for the dissociation of ammonium chloride (Trans., 1894, **65**, 616), mercurous chloride, and other substances (Trans., 1900, **77**, 645), led us to investigate the question whether, in the dried condition, nitrogen trioxide could be obtained in the gaseous state.

In order to obtain the liquid available for experiment, it was necessary to seal it up in bulbs without contact with atmospheric moisture. In order to do this, a series of ten bulbs was blown on a thin capillary tube the outside diameter of which was about 0·5 mm. The end of this tube was sealed to a tube of about 20 c.c. capacity, and the whole dried by heating while a current of dried air was drawn through. A plug of ignited asbestos was placed in the junction of the capillary and the wide tube, and plugs of redistilled phosphorus pentoxide introduced. The tube was closed and allowed to stand for a week to ensure the drying of the internal surface of the glass. The nitrogen trioxide was prepared by the action of nitric acid (sp. gr. 1·3) on arsenic trioxide. The gas was passed first through a long worm tube cooled by ice in order to condense any nitric acid carried over. It was then dried by a tube of phosphorus pentoxide, and condensed in the tube described above, which was cooled by pounded ice and calcium chloride. When sufficient liquid had been condensed, a current of nitric oxide, dried by phosphorus pentoxide, was bubbled through it for an hour, and the tube sealed. It was left to dry for three weeks. By cooling the bulbs, the liquid distilled over, and by means of a very fine-pointed blow-pipe flame the capillaries between the bulbs were drawn off, and the bulbs containing the liquid were washed in distilled water and dried in a desiccator. The sealing off of these bulbs was an operation of extreme delicacy, and many attempts resulted in failure. Sealing by means of a fine, red-hot platinum wire was tried, but the method left the ends of the capillaries so thin that they burst when the liquid attained the ordinary temperature.

Many methods were tried before a satisfactory analysis of the liquid could be obtained. Potassium permanganate, potassium iodide, ammonia, and carbamide solution were all tried as reagents for estimating the oxygen or nitrogen, and failed to give constant results. This was also the case with the ordinary nitrometer method with mercury and sulphuric acid, the volume of the nitric oxide evolved being always too small. A possible explanation of the latter fact is that nitric oxide is not the only gas produced. In one experiment, the gas was transferred to another nitrometer and showed considerable contraction when treated with alcohol, and the residue was not all absorbed by ferrous sulphate solution, indicating the presence of nitrogen and nitrous oxide. A direct method was then resorted to. A weighed bulb of the liquid was introduced into a thick-walled Jena glass tube with a piece of glass rod for breaking it. In the other end was placed a weighed roll of copper gauze enclosed in a thin-walled Jena tube open at both ends. The wider tube was then drawn out at each end, filled with dried nitrogen and sealed. The bulb was broken and the part of the tube containing the copper was heated in an improvised furnace for twelve hours. By breaking the capillary end of the wider tube in a thick-walled indiarubber tube, the excess of nitrogen was made to displace water from a wash-bottle into a weighed flask, thus giving a rough estimation of the nitrogen in the trioxide. This estimation must always give results which are too low, since the sealing of the tube, however carefully done, must heat and expand some of the original nitrogen. If it had been possible to use large quantities of the liquid, the error would have been minimised, but attempts to do this led to the explosion of the whole. The oxygen was estimated by the gain in weight of the copper. The results were:

	Weight of liquid.	Increase in weight of copper.	Percentage of nitrogen.	Percentage of oxygen.
1.	0·0856	0·0540	—	63·0
2.	0·1875	0·1189	35·1	63·4
3.	0·1076	0·0667	33·8	62·1
4.	0·0937	0·05980	33·9	63·8
5.	0·1145	0·0722	34·7	63·1

The mean percentage of oxygen is 63·08, that calculated for N_2O_3 is 63·17.

In order to show that the deficiency of nitrogen is really caused as stated above, and not by the presence of dissolved phosphorus pentoxide, a large quantity of the liquid was dissolved in cooled nitric acid, but this produced no colour with ammonium molybdate. The liquid also evaporated in air without leaving any residue. Its composition therefore corresponds to the formula N_2O_3.

In order to determine the density of the gas evolved by the evaporation of the liquid, weighed bulbs were broken in a Lunge's nitrometer over purified and dried mercury. The breaking of the bulb was effected by the pressure of a long glass rod which passed through an indiarubber stopper at the bottom of the nitrometer. The gas has very little effect on dried mercury. The following results were obtained by this method:

	Weight of liquid used.	Time of drying over phosphorus pentoxide.	Temperature.	Pressure.	Density.
1.	0·0645	6 days	15°	770 mm.	43·2
2.	0·0274	27 ,,	14	747 ,,	43·6
3.	0·0515	13 ,,	13	768 ,,	48·6

On adding concentrated sulphuric acid to the gas, solution took place so rapidly that the rush of the mercury up the tube could not be followed by the eye, and the impact of the metal against the top of the tube threatened its destruction. This observation makes it clear that the gas does not contain a mixture of nitrogen peroxide and nitric oxide, which is shown by experiment to undergo only a comparatively slow absorption by sulphuric acid.

Other determinations of the density of the gas were made in a special form of V. Meyer's apparatus, which has been described by one of us (Trans., 1900, **77**, 647). The weighed bulb of liquid was placed at the bottom of the cylindrical bulb of the apparatus and the movable glass spoon was used to support a piece of heavy glass rod. On turning the spoon, the rod dropped on to the bulb, so liberating the liquid. In order that the rod should hit the bulb, it was found necessary to seal a perforated glass tube inside the apparatus to act as a guide. The apparatus was dried by heating while a current of nitrogen was passed through. The sealed tube which formed the stopper of the apparatus contained phosphorus pentoxide, and the exit tube, which was connected with a gas measuring apparatus, was filled with the same substance. The drying of the apparatus by the phosphorus pentoxide was continued through varying periods as shown in the table on page 1865.

The density of undissociated N_2O_3 is 38, and hence the gas obtained in these experiments must contain a higher polymeride, probably N_4O_6, corresponding to the analogous oxides of phosphorus and arsenic. It will be noticed that there is a large variation in the densities obtained in the different experiments, and it should be mentioned that the bulbs used came from not less than eight different preparations, the liquid in which was condensed at different temperatures, and which was allowed different lengths of time to dry in contact with the phosphorus pentoxide. We hope that it

No.	Weight of liquid.	Time of drying of the vapour density apparatus in days.	Temperature.	Pressure in mm.	Density.
1.	0·0649	23	22°	768	38·1
2.	0·0593	4	21	744	38·4
3.	0·0241	14	22	762	41·5
4.	0·0487	6	20	735	42·0
5.	0·0160	6	16	756	42·1
6.	0·0902	20	18	757	42·8
7.	0·0452	6	22	745	42·8
8.	0·0382	14	20	744	49·0
9.	0·1034	8	18	756	49·3
10.	0·0299	28	21	742	57·0
11.	0·1475	22	17	802	59·2
12.	0·0493	7	18	739	59·8
13.	0·0134	33	60	613	62·2

may be possible by drying the liquid at a lower temperature to obtain the higher polymeride in a pure condition.

In order to compare the behaviour of the dried and undried liquid, the same apparatus was used for determining the density of the liquid which had been contaminated by a trace of moisture. This was effected by opening the capillary of the bulb, immersed in a freezing mixture, for a few seconds and then sealing it up. The first difference noted during the density determination was that the boiling liquid rapidly lost its green colour, leaving a yellow liquid which then disappeared, whilst with the dried liquid there was no change in colour as it boiled away. The density given by this moist liquid was 28·2, the temperature being 22°. If it is calculated what density would be given by N_2O_3 breaking up into N_2O_4, NO_2, and NO at 22°, a density of 27·8 is found, so that in presence of a mere trace of moisture practically complete dissociation of the liquid takes place.

Some determinations of the molecular weight by the lowering of the freezing point of purified and dried benzene were made, to see if at the temperature of 4° and in solution the higher polymeride would be in a more concentrated state. This was not found to be the case. Two bulbs from the same preparation were used in the first case, and one from another preparation in the second.

I. (*a*) 0·1364 of liquid in 10·2 of benzene gave depression 0·8°.
M.W. = 83.
(*b*) 0·0455 of liquid in 10·3 of benzene gave depression 0·26°.
M.W. = 83·2.
II. 0·0627 of liquid in 10·8 of benzene gave depression 0·29°.
M.W. = 95.

In these experiments, the benzene was dried over distilled phosphorus pentoxide, and care was taken that the thermometer and the tube in which the experiment was done were as far as possible dried to a similar extent. The dried benzene was quite unaffected by the dried trioxide. After a very short exposure to moist air, the solution lost its green colour, at the same time giving off nitric oxide with effervescence, leaving a yellow solution of nitrogen peroxide.

We hope in a future communication to describe the physical and chemical properties of nitrogen trioxide. Its specific gravity in the state of liquid is about 1·11. The liquid has a green colour at the ordinary temperature, but, when cooled to $-2°$ or below, the colour changes to a deep indigo-blue. The liquid shows no signs of freezing in a mixture of solid carbon dioxide and ether at $-81°$, but in liquid air it forms very deep blue crystals. It is very little, if at all, soluble in water. When a bulb is broken under ice-water, the liquid sinks to the bottom of the vessel, giving off nitric oxide and nitrogen peroxide, the latter dissolving in the water. The gas is very soluble indeed in concentrated sulphuric acid.

Addendum.

In order to ascertain if similar polymerisation takes place with nitric oxide and carbon monoxide, these gases were introduced into tubes containing phosphorus pentoxide, which were connected with manometers. The tubes were then cooled with liquid air, so that the liquefied gases were in contact with the drying agent. The drying at the low temperature was continued for four days. On regaining the ordinary temperature, the gases showed no change in volume, so that in these circumstances no polymerisation takes place.

The work has been done in the new research laboratory at Christ Church.

Christ Church,
Oxford.

CLXXX.—*The Decomposition of Hyponitrous Acid in Presence of Mineral Acids.*

By Prafulla Chandra Rây and Atul Chandra Gañguli.

Hyponitrous acid has been isolated by Hantzsch and Kaufmann, who have also described some of its important properties and its decomposition products (*Annalen*, 1896, **292**, 317). In continuation of our work on the decomposition of silver and mercurous hyponitrites we have recently studied the action of mineral acids on these salts at the ordinary temperature, namely, 25—29°. It will be shown that the hyponitrous acid which is set free decomposes simultaneously according to the two equations:

$$2HNO = H_2O + N_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$5HNO = 2H_2O + HNO_3 + 2N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Silver Hyponitrite and Nitric, Hydrochloric, and Sulphuric Acids.

Method of Experiment.—In order to avoid unnecessary repetition the details of experiments will be given here once for all. The substance was weighed in a tube, and another tube, much narrower in diameter, and containing from 1 to 2 c.c. of dilute nitric acid, was placed in it. The apparatus, after exhaustion by means of a Sprengel pump, was gently tilted so as to bring the salt and the acid into contact with each other. Brisk effervescence at once set in. The gaseous product which was found to be free from nitric oxide was analysed in the following manner. It was repeatedly shaken up with tap water,* changing the water if necessary, until no more absorption took place. The remaining gas which was unaffected by alkaline pyrogallate was taken to be nitrogen. The residue in the tube did not respond to Nessler's or Fehling's solution and was thus absolutely free from ammonia and hydroxylamine. It was also found to be free from nitrite. The amount of nitrate in it was estimated by making it up to a given volume and treating an aliquot portion by the Crum-Frankland method. An example will make the point clear. Let us assume that the first reaction which set free hyponitrous acid was according to the equation:

$$5AgNO + 5HNO_3 = 5AgNO_3 + 5HNO \quad . \quad . \quad . \quad (1)$$

and that the second reaction which gave rise *de novo* to nitric acid was that conforming to:

$$5HNO = HNO_3 + 2H_2O + 2N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In the experiment in question 1 c.c. of dilute nitric acid was used. As a blank test, 1 c.c. of this acid was made up to 20 c.c., of which 1 c.c. again gave 3·9 c.c. of nitric oxide. The residual product was also made up to the same bulk (20 c.c.) and 1 c.c. of it yielded 4·1 c.c. of nitric oxide. The difference was 0·2 c.c. of nitric oxide. Now (20 × 0·2) c.c. or 4 c.c. was the total amount of nitric oxide and half of it, namely, 2 c.c., as nitrogen, represented the nitric acid generated according to the equation (2). The free nitrogen which was measured according to the process described above was actually found to be

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* That is, with water saturated with respect to nitrogen at the ordinary temperature and pressure. By blank experiments we have satisfied ourselves that it is a fairly trustworthy method of estimating the proportion of nitrous oxide and nitrogen in a mixture of the two gases.

8·2 c.c. at the same temperature and pressure; hence the ratio of nitrogen in nitric acid to nitrogen in the free condition was as 1 : 4. When sulphuric or hydrochloric acid was used no blank experiment was, of course, necessary.*

Decomposition of Silver Hyponitrite.

(*a*) *With nitric acid* (1 c.c. = 0·179 gram of HNO_3).

Expt. I.—0·1764 gave 11·5 c.c. N as such, 2·88 c.c. N as HNO_3, and 2·0 c.c. N_2O; † $t = 25°$; $p = 760$ mm.

Expt. II.—0·1016 gave 6·1 c.c. N as such, 1·5 c.c. N as HNO_3, and 1·9 c.c. N_2O; $t = 25°$; $p = 760$ mm.

Expt. III.—0·1218 gave 8·2 c.c. N as such, 2·05 c.c. N as HNO_3, and 1·3 c.c. N_2O; $t = 27°$; $p = 760$ mm.

(*b*) *With hydrochloric acid* (1 c.c. = 0·153 gram of HCl).

Expt. I.—0·2144 gave 13·4 c.c. N as such, 3·4 c.c. N as HNO_3, and 3·1 c.c. N_2O; $t = 26°$; $p = 760$ mm.

(*c*) *With sulphuric acid* (1 c.c. = 0·366 gram of H_2SO_4).

Expt. I.—0·17 gave 5·2 c.c. N as such, 1·3 c.c. N as HNO_3, and 8·7 c.c. N_2O; $t = 27°$; $p = 760$ mm.

Expt. II.—0·115 gave 4·8 c.c. N as such, 1·2 c.c. N as HNO_3, and 4·9 c.c. N_2O; $t = 31°$; $p = 760$ mm.

The results of these experiments are tabulated below; the figures denote percentages:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
(*a*). With nitric acid:					
I.	7·25	1·81	1·26	10·32	10·14
II.	6·72	1·65	2·09	10·46	,,
III.	7·45	1·86	1·18	10·49	,,
(*b*). With hydrochloric acid:					
I.	6·95	1·74	1·61	10·30	10·14
(*c*). With sulphuric acid:					
I.	3·39	0·85	5·70	9·94	10·14
II.	4·52	1·13	4·58	10·23	,,

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* It may be noted here that as the Crum-Frankland method is not satisfactory in presence of a chloride the nitric acid in this case was tested by Pelouze's method.

† The gases were always measured in the moist state.

Mercurous Hyponitrite and Nitric, Sulphuric, and Hydrochloric Acids

The method of experiment was the same as described before, and no further prefatory remarks are called for. The only point to bear in mind is that a solution of mercurous hyponitrite in dilute nitric acid undergoes slow dissociation; thus: $Hg_2(NO)_2 = Hg + Hg(NO)_2$. As the acid was very dilute and as the reaction was completed in a few minutes there was no appreciable disturbance due to secondary reaction, namely, interaction between metallic mercury and excess of free nitric acid.

Decomposition of Mercurous Hyponitrite.

(*a*) *With nitric acid.*

Expt. I.—0·197 gave 6·3 c.c. N as such, 1·58 c.c. N as HNO_3, and 1·0 c.c. N_2O; $t = 28°$; $p = 760$ mm.

(*b*) *With hydrochloric acid.*

Expt. I.—0·115 gave 4·0 c.c. N as such, 1·0 c.c. N as HNO_3, and 1·6 c.c. N_2O; $t = 31°$; $p = 760$ mm.

Expt. II.—0·25 gave 9·3 c.c. N as such, 2·33 c.c. N as HNO_3, and 2·4 c.c. N_2O; $t = 30°$; $p = 760$ mm.

(*c*) *With sulphuric acid.*

Expt. I.—0·1955 gave 2·8 c.c. N as such, 0·7 c.c. N as HNO_3, and 5·2 c.c. N_2O; $t = 25°$; $p = 760$ mm.

The results are presented below in percentages in a tabulated form:

(*a*). With nitric acid:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
I.	3·55	0·89	0·56	5·0	6·09

(*b*). With hydrochloric acid:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
I.	3·76	0·94	1·51	6·21	6·09
II.	4·05	1·01	1·05	6·11	„

(*c*). With sulphuric acid:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
I.	1·60	0·4	2·98	4·98	6·09

NOTE.—The preparation and analysis of the samples of salts made use of in the experiments recorded in the above tables have been given at length in the previous memoirs on "Mercurous Hyponitrite" and "The Decomposition of Mercurous and Silver Hyponitrites by Heat" (this vol., pp. 1404, 1399).

Discussion of Results.

It will be seen that silver hyponitrite by reaction with the three mineral acids gives almost the theoretical yield of hyponitrous acid, which again breaks up into nitrous oxide, nitrogen, and nitric acid. According to Hantzsch and Kaufmann, ammonia and nitrous acid are among the decomposition products of hyponitrous acid, but under certain conditions they failed to detect either of these, obtaining instead traces of nitric acid, as, for instance, when they allowed hyponitrous acid to remain for twenty-four hours in contact with a few drops of hydrochloric acid. As these chemists contented themselves with proving, merely qualitatively, the existence of nitric acid, they erroneously concluded that it was derived from the oxidation of nitrous acid.* In fact, the following three sets of reactions are strictly comparable:

$$5HNO = HNO_3 + 2N_2 + 2H_2O,\dagger$$
$$3KClO = KClO_3 + 2KCl,$$
$$2H_3PO_2 = H_3PO_4 + PH_3.$$

When chlorine is passed into a hot concentrated solution of potassium hydroxide, the hypochlorite which may be taken to be potentially formed at once passes into compounds which are stable under the existing conditions. Hypophosphorous acid, again, is only stable at a low temperature; on being heated it gives rise to phosphoric acid and phosphine. In these two instances the oxidation does not stop short at the intermediate stage of chlorite or phosphite.

One remarkable feature is the behaviour of sulphuric acid, which invariably ensures a larger yield of nitrous oxide. It is evident that the presence of mineral acids has a specific directive influence in determining the course which the reaction follows.

As regards mercurous hyponitrite, the mechanism of the reaction is substantially the same as with its silver analogue. It is noteworthy, however, that the decomposition of this salt by means of sulphuric and nitric acids is never complete. In other words, silver hyponitrite is decomposed with equal readiness by both the oxygen and haloid acids, but the mercurous salt only by the latter.

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* "Sondern Salpetersäure (durch Oxydation der Salpetrigen Säure entstanden)," *loc. cit.*, 333.

† Thum has shown that an aqueous solution of hyponitrous acid is directly oxidised to nitric acid by means of potassium permanganate. The three instances cited above are, however, those of autoxidation and reduction.

CLXXXI.—*Contributions to the Chemistry of the Terpenes. Part II. The Oxidation of Limonene with Chromyl Chloride.*

By George Gerald Henderson.

The action of chromyl chloride on limonene is violent, but when moderated by dissolving each of these substances in a large quantity of carbon disulphide it results in the formation of a solid *additive product*, $C_{10}H_{16},2CrO_2Cl_2$. This compound is decomposed by water with evolution of heat, chromic chloride passing into solution, and a brown, oily liquid, together with a quantity of resinous matter, separating. When the liquid oxidation product is purified by distillation in a current of steam, a further quantity of resinous matter is left in the distilling flask, and a yellow oil passes over. This oil contains at least three substances: an aldehyde, a ketone, and a smaller quantity of some chlorinated oxidation product, which, however, on account of its instability, could not be isolated. The *aldehyde*, $C_{10}H_{14}O$, which was separated by conversion into the crystalline *compound* which it forms with sodium hydrogen sulphite, is a colourless, oily liquid with a strong odour. It is unsaturated, and on exposure to air it undergoes oxidation to a crystalline *acid*, $C_{10}H_{14}O_2$. The *silver* salt of the acid crystallises from water, in which it is sparingly soluble, in white needles. When the aldehyde is oxidised by heating with dilute nitric acid, it does not yield the acid $C_{10}H_{14}O_2$, but is converted into *p*-toluic acid. *p*-Toluic acid is also the principal product obtained when the aldehyde is oxidised with a dilute solution of potassium permanganate. The *semicarbazone* of the aldehyde crystallises from methyl alcohol in glistening leaflets. The *ketone*, $C_9H_{12}O$, which is the main constituent of the oxidation product, is an oily liquid with a faint yellow colour and a characteristic odour. It is unsaturated. The *semicarbazone* of the ketone crystallises from methyl alcohol in lustrous prisms, which contain one molecule of methyl alcohol, and which effloresce quickly when exposed to air, yielding a white powder. When heated with ammonium formate, the ketone is converted into the formyl derivative of an *amine*, $C_9H_{13}\cdot NH_2$. The amine is a colourless liquid with a disagreeable odour, and is almost insoluble in water. Its hydrochloride and sulphate are deliquescent, and are extremely easily soluble in water or alcohol; its *platinichloride*, which is sparingly soluble, forms brownish-yellow crystals.

Unfortunately, the yields are very small, and the quantities of the aldehyde and the ketone hitherto obtained have not permitted of a full examination of these substances. However, enough has been done to show that, under suitable conditions, limonene behaves with chromyl chloride similarly to pinene (Trans., 1903, **83**, 1299), at least to the extent that the solid additive compound which is formed from each of the hydrocarbons is decomposed by water with the formation in each case of an aldehyde, a ketone, and a product containing chlorine as well as oxygen. It is intended to continue the investigation of these substances.

EXPERIMENTAL.

Oxidation of the Hydrocarbon.

For the first oxidation experiments, *i*-limonene (dipentene) was prepared from oil of bitter orange. The oil was agitated with aqueous sodium carbonate and then with water, dried, and distilled. The portion which distilled at 174—178° was mixed with half its volume of glacial acetic acid, and dry hydrogen chloride was passed slowly over the mixture, which was kept cool with ice, and was shaken at intervals. After some days the mixture solidified; water was added, and the crystalline dipentene dihydrochloride which separated was collected and purified by solution in a small quantity of alcohol and precipitation with water. A mixture of the dihydrochloride with an equal weight of anhydrous sodium acetate and twice its weight of glacial acetic acid was boiled under a reflux condenser for half an hour, and the liberated hydrocarbon was then distilled off with a current of steam. The impure hydrocarbon was collected, boiled for some time under a reflux condenser with dilute aqueous potassium hydroxide, distilled over with steam, dried, and fractionated. Almost the whole of it distilled at 175—176°. In later experiments, *d*-limonene, also prepared from oil of bitter orange, was used. The oil was shaken with a solution of sodium carbonate, distilled in a current of steam, collected, dried, and finally fractionated with the aid of a "pear" still-head. In this way, a large fraction was obtained which boiled constantly at 175—176°.

The oxidation of the limonene was effected in a similar manner to that of pinene (*loc. cit.*). A 10 per cent. solution of chromyl chloride (2 mols.) in pure, dry carbon disulphide was added slowly to a similar solution of limonene (1 mol.), the flask containing the latter being cooled with ice-water and constantly shaken. The dark brown precipitate which slowly settled was collected, washed with carbon disulphide, and while still mixed with some of that liquid, with which it forms a pasty mass, thrown in small quantities at a time into ice-cold water, the mixture being well shaken after each addition. A little sulphurous acid was added to the water, in order to reduce any chromic acid which might be formed during the decomposition of the additive product. When the action was completed, the oxidation product was extracted by means of carbon disulphide; a considerable quantity of a brown, resinous substance was left undissolved. The carbon disulphide solution was well washed with water and dried with calcium chloride, and, after removal of the solvent, the brown, oily residue was purified by distillation with steam. More resinous matter was left in the distilling flask, and the clear, yellow oil which passed over was separated from the water by means of ether.

The *additive compound*, $C_{10}H_{16},2CrO_2Cl_2$, which is formed by the action of chromyl chloride on limonene, is, when dry, a powder of a greyish-brown colour, which on heating evolves hydrogen chloride. On exposure to the air, it quickly begins to absorb moisture and to decompose, and it reacts at once with water, yielding a viscous, brown liquid insoluble in water, a quantity of resinous matter insoluble in carbon disulphide, and a solution containing chromic chloride and usually a little chromic acid.

Preparation of the Aldehyde, $C_{10}H_{14}O$.

The ethereal solution of the purified oxidation product was concentrated to small bulk, and shaken with a freshly-prepared saturated solution of sodium hydrogen sulphite. The additive compound, $C_{10}H_{14}O,NaHSO_3$, which slowly separated in small, shining crystals, was collected and washed with alcohol and with ether, and the ethereal solution of the residual oil was again shaken with a fresh quantity of the bisulphite solution. This process was repeated until no more crystals formed, even after a period of several days, when it was considered that the aldehyde was completely removed from the original solution. The purified bisulphite compound was mixed with aqueous sodium carbonate, and the liberated aldehyde was distilled off in a current of steam and extracted from the distillate with ether. The ethereal solution was dried with calcium chloride, and, after removal of the ether, the aldehyde was purified by fractional distillation under diminished pressure in a current of dry carbon dioxide. From the filtrates obtained during the preparation and purification of the bisulphite compound, which is fairly readily soluble in water and in alcohol, a further quantity of less pure aldehyde was obtained, after removal of the ether and alcohol, by addition of sodium carbonate and distillation with steam.

The *aldehyde* thus obtained from limonene is an almost colourless, oily liquid with a strong, peculiar odour. It is practically insoluble in water, but dissolves freely in alcohol or ether; it boils at 221—222° under a pressure of 755 mm. It shows the characteristic reactions of aldehydes, giving a crystalline bisulphite compound, reducing ammoniacal solutions of silver salts, restoring the colour to magenta decolorised with sulphurous acid, and forming a crystalline semicarbazone. It is unsaturated, as it at once unites with bromine dissolved in dry chloroform, yielding an unstable additive compound, which quickly decomposes and evolves hydrogen bromide. It undergoes oxidation when exposed to the air. The results of several analyses pointed to the formula $C_{10}H_{14}O$.

The *semicarbazone* of the aldehyde, $C_{10}H_{14}{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, prepared in the usual manner, crystallises in small, lustrous leaflets which melt at 156—157°. It is fairly readily soluble in cold, easily so in hot methyl alcohol:

0·1021 gave 17·8 c.c. of nitrogen at 19° and 765 mm. N = 20·6.
0·2020 ,, 36 c.c. ,, ,, 20° ,, 765 mm. N = 20·7.
$C_{11}H_{17}ON_3$ requires N = 20·3 per cent.

Preparation of the Acid, $C_{10}H_{14}O_2$.

When exposed to the air, the aldehyde was gradually converted through oxidation into a soft, semicrystalline mass. This was warmed with a solution of sodium carbonate, and the solution was extracted several times with ether, in order to remove unchanged aldehyde, and then acidified. The acid, which separated in an oily state, was extracted by means of ether, and, after removal of the ether, was purified by repeated crystallisations from slightly diluted methyl alcohol. The process of purification was troublesome on account of the tendency of the *acid* to separate in an oily state, but it was finally obtained in small, colourless crystals which melt at 172°. It is very readily soluble in alcohol and in ether, but practically insoluble in water, and it is hardly, if at all, volatile in a current of steam.

The quantity of the purified acid available being too small for analysis, it was converted into the *silver* salt, $C_{10}H_{13}O_2Ag$. This salt was precipitated from a solution of the ammonium salt as a white, crystalline powder, and was purified by crystallisation from water, from which it separates in small, white prisms. It is fairly readily soluble in hot, but sparingly so in cold, water:

0·3278 gave 0·1292 Ag. Ag = 39·4.
$C_{10}H_{13}O_2Ag$ requires Ag = 39·6 per cent.

When the aldehyde is boiled for some time with dilute nitric acid, it is oxidised to an acid different from that just described. This acid, after purification by crystallisation from light petroleum, melts at 178°. It separates from aqueous solution in small, colourless needles. It dissolves very easily in alcohol or ether, fairly readily in hot water, and very sparingly in hot light petroleum, and it volatilises, although rather slowly, in a current of steam. It is saturated, since it does not reduce potassium permanganate and does not form an additive compound with bromine. In all these properties, this acid corresponds very closely with *p*-toluic acid, and its identity with the latter was established by analysis of the acid itself and of its silver salt:

0·1592 gave 0·4114 CO_2 and 0·0886 H_2O. C = 70·5; H = 6·2.
$C_8H_8O_2$ requires C = 70·6; H = 5·9 per cent.

The silver salt was obtained as a white, crystalline precipitate, which was thoroughly washed and dried:

0·3992 gave 0·1770 Ag. Ag = 44·3.
$C_8H_7O_2$ Ag requires Ag = 44·4 per cent.

If the aldehyde is oxidised with a 2 per cent. solution of potassium permanganate, the chief product, even in the cold, is again *p*-toluic acid, but if a considerably more dilute solution of the reagent is employed, some of the acid, $C_{10}H_{14}O_2$, is also obtained. It is evident that this acid is easily converted into *p*-toluic acid by oxidation.

Preparation of the Ketone, $C_9H_{12}O$.

The ethereal solution of the oxidation products of limonene, from which the aldehyde had been removed as described above, was washed with a solution of sodium carbonate and then with water, dried, and heated until the ether was removed. Preliminary examination of the oily residue showed that, in addition to the ketone, it contained a smaller quantity of a chlorinated substance. It was found impossible to isolate the latter, because treatment of the mixture with solvents did not effect a separation, whilst on distillation, even when the pressure was reduced to 15 mm., it began to decompose with liberation of water and hydrogen chloride. Since the presence of this chlorinated compound rendered the purification of the ketone difficult, the mixture of substances was treated with alcoholic potash in sufficient quantity to decompose it, and, after removal of the precipitate of potassium chloride, which was formed almost at once, the filtrate was mixed with water and extracted several times with ether. The ethereal solution was separated, well washed with water, and dried over calcium chloride, the ether was removed, and the residual oil was distilled at 15 mm. in a current of dry carbon dioxide. After repeated distillations, a large fraction, which boiled constantly at 112—113°, was obtained.

The *ketone* is an oily liquid with a faint yellow colour and a camphor-like odour. It dissolves readily in the usual organic solvents, but is insoluble in water. It does not unite with sodium hydrogen sulphite, but forms a crystalline semicarbazone. It is unsaturated, combining at once with bromine in chloroform solution, but the additive product which is formed is unstable, and begins to evolve hydrogen bromide almost at once. The boiling point of the ketone is 112—113° under a pressure of 15 mm.:

0·1090 gave 0·3155 CO_2 and 0·0930 H_2O. C = 79; H = 9·5.
0 1366 „ 0·3950 CO_2 „ 0·1150 H_2O. C = 78·9; H = 9·3.
$C_9H_{12}O$ requires C = 79·4; H = 8·8 per cent.

The *semicarbazone* of the ketone, $C_9H_{12}{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, was prepared in the usual way and purified by crystallisation from methyl alcohol. It separates from that solvent in clusters of lustrous, transparent needles, but the crystals, when exposed to the air, rapidly become opaque, and are then easily crushed to a white powder. Analysis showed that the needle-shaped crystals contain one molecule of methyl alcohol of crystallisation, which is quickly lost at the ordinary temperature. After being heated to 100° in order to expel all the methyl alcohol, the semicarbazone melts at 205°. It is only moderately soluble in hot, and very sparingly so in cold, methyl alcohol:

0·1378 gave 27 c.c. nitrogen at 20° and 752 mm. N = 22·2.
0·1440 „ 27·9 c.c. „ „ 19° „ 758 mm. N = 22·2.
$C_{10}H_{15}ON_3$ requires N = 21·8 per cent.

In order to determine the proportion of methyl alcohol of crystallisation, the crystals were quickly pressed in bibulous paper, weighed, and heated at 105°:

0·8555 lost 0·1236. MeOH = 14·4.
$C_{10}H_{15}ON_3,CH_3{\cdot}OH$ requires MeOH = 14·3 per cent.

Preparation of the Amine, $C_9H_{13}{\cdot}NH_2$.

The ketone, mixed with twice its weight of dry ammonium formate, was heated at 165° in a sealed tube for twelve hours. The contents of the tube were treated with ether, the solution was filtered, the ether was removed, and the residue, consisting mainly of the formyl derivative of the amine, was hydrolysed by heating for about twelve hours with excess of alcoholic potash under a reflux condenser. Water was then added, the moisture was shaken several times with ether, and the ethereal solution was washed with water and then shaken with dilute hydrochloric acid. The solution of the hydrochloride of the amine was mixed with excess of potassium hydroxide and the liberated amine was distilled off with a current of steam. The distillate was neutralised with hydrochloric acid, and, after evaporation of the solution to dryness on the water-bath, the hydrochloride of the amine was obtained as a deliquescent, crystalline mass. It is extremely easily soluble in water and in alcohol, and from alcoholic solution is precipitated by ether in the form of a syrupy liquid which showed no signs of becoming crystalline even after long standing under ether. The sulphate and the nitrate of the amine are also easily soluble, deliquescent substances, but the platinichloride is very sparingly soluble in water.

The *amine*, of which the quantity obtained was unfortunately very small, is a colourless liquid with a disagreeable odour and an alkaline reaction. It is almost insoluble in water, but readily soluble in alcohol or ether, and it volatilises easily in steam. The *platinichloride* of the amine crystallises in small, brownish yellow needles, and is sparingly soluble in hot water:

0·1032 gave 0·0290 Pt. Pt = 28·1.

$(C_9H_{13}NH_2)_2,H_2PtCl_6$ requires Pt = 28·5 per cent.

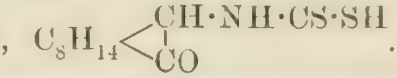
I am indebted to Mr. W. T. Munro and to Mr. J. A. Campbell, A.I.C., for assistance with part of this work, and to the Committee of the Carnegie Trust for a grant in defrayal of the expense.

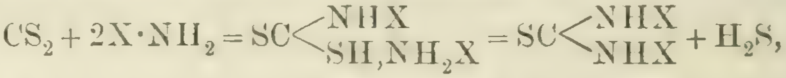
CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CLXXXII.—*Studies in the Camphane Series. Part XXIV. Camphoryldithiocarbamic Acid and Camphorylthiocarbimide.*

By MARTIN ONSLOW FORSTER and THOMAS JACKSON.

WHEN bornylcarbimide was obtained by the action of nitrous acid on bornylcarbamide (Forster and Attwell, Trans., 1904, **85**, 1188), it was hoped that the resolution of racemic alcohols might be effected by converting these into a mixture of carbamates, separable by fractional crystallisation, but the comparative indifference of bornylcarbimide towards alcohols precludes its application to this problem. Since then, however, Pickard and Littlebury (Trans., 1906, **89**, 467) have accomplished the division of racemic α-phenyl-α'-4-hydroxyphenylethane by means of *l*-menthylcarbimide, and it is probable that *d*-camphorylcarbimide (Forster and Fierz, Trans., 1905, **87**, 110) could be used for a similar purpose, as it has the property of yielding urethanes with simple alcohols. The production of these carbimides, however, presents certain difficulties, and it seemed desirable to ascertain whether an optically active thiocarbimide could not be prepared more readily, and applied for the purpose indicated. Unsuccessful experiments with this object had been made with bornylamine (Forster and Attwell, *loc. cit.*), and we therefore proceeded to study the possibilities of aminocamphor in the hope that dicamphorylthiocarbamide might be made to yield camphoryl mustard oil by a process analogous to the well-known transformation of diphenylthiocarbamide into phenylthiocarbimide.

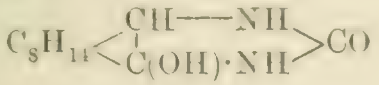
On heating an ethereal solution of aminocamphor with carbon disulphide, however, we were surprised to find that hydrogen sulphide is not set free, owing to the remarkable stability of camphoryldithiocarbamic acid,  $C_8H_{14}\left<\begin{array}{l}CH\cdot NH\cdot CS\cdot SH\\ | \\ CO\end{array}\right.$. The usual result of treating an aliphatic amine with carbon disulphide is the formation of alkylamine alkyldithiocarbamate, which gradually breaks up into dialkylthiocarbamide and hydrogen sulphide,



$$CS_2 + 2X\cdot NH_2 = SC\left<\begin{array}{l}NHX\\ SH,NH_2X\end{array}\right. = SC\left<\begin{array}{l}NHX\\ NHX\end{array}\right. + H_2S,$$

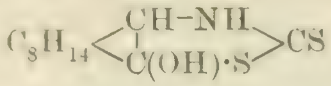
and this is the course which bornylamine follows. In the aromatic series, the intermediate stage is not observed, aniline phenyldithiocarbamate, for instance, losing hydrogen sulphide too quickly to permit of its being isolated, although Losanitsch (*Ber.*, 1891, **24**, 3021; 1907, **40**, 2970) has shown that if the action of carbon disulphide on aniline is conducted in presence of ammonia, elimination of hydrogen sulphide may be arrested, and the ammonium salt of phenyldithiocarbamic acid produced. The literature shows that a variety of aliphatic amines have been treated with carbon disulphide, but in no case, so far as we have been able to ascertain, has the dithiocarbamic acid been isolated; the aromatic representatives, also, would appear to be most unstable, phenyldithiocarbamic acid, for example, having been described as changing immediately into thiocarbanilide, hydrogen sulphide, and carbon disulphide (Rathke, *Ber.*, 1878, **11**, 958).

The stability of camphoryldithiocarbamic acid appears therefore to be unique, and the nearest approach to its properties is furnished by phenyldithiocarbazinic acid, $C_6H_5\cdot NH\cdot NH\cdot CS\cdot SH$, the phenylhydrazine salt of which was described by E. Fischer (*Annalen*, 1878, **190**, 115). Busch records a definite melting point for the free acid (*Ber.*, 1895, **28**, 2639), but Busch and Ridder (*Ber.*, 1897, **30**, 845) describe the substance as somewhat unstable, in part changing into phenylhydrazine phenyldithiocarbazinate, whilst the remainder undergoes a more profound decomposition and becomes black. No change of this character has been observed in connexion with camphoryldithiocarbamic acid, a colourless, crystalline specimen of which has now been exposed to diffused light during more than six months without altering in appearance or developing any odour. In speculating as to the cause of this stability, we were naturally led to ascribe it to the neighbourhood of the carbonyl group, and, in view of the isomerism observed in connexion with camphorylcarbamide (Forster and Fierz, *loc. cit.*), considered the possibility of representing it as a pseudo-modification of the normal dithiocarbamic acid:



$$C_8H_{14}<\begin{array}{l}CH{—}NH\\ C(OH)\cdot NH\end{array}>CO$$

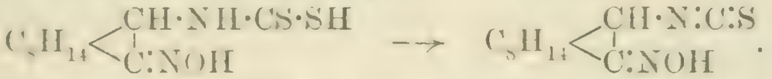
Camphoryl-ψ-carbamide.



$$C_8H_{14}<\begin{array}{l}CH{-}NH\\ C(OH)\cdot S\end{array}>CS$$

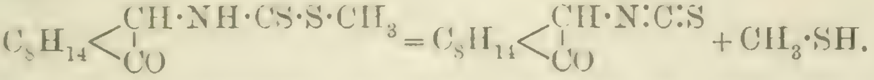
Camphoryl-ψ-dithiocarbamic acid.

For several reasons, however, this explanation appears most unlikely. In the first place, the substance is a strong acid, and also differs from camphoryl-ψ-carbamide in its failure to yield a nitroso-derivative. Furthermore, the oxime of camphoryldithiocarbamic acid, prepared by the action of carbon disulphide on aminocamphoroxime, although capable of a separate existence, readily loses hydrogen sulphide, passing into the oxime of camphorylthiocarbimide:



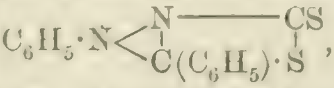
$$C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot CS\cdot SH\\ C{:}NOH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot N{:}C{:}S\\ C{:}NOH\end{array}.$$

Finally, the methyl ester of camphoryldithiocarbamic acid, a colourless substance melting sharply at 147° without liberating gas, breaks up at about 170°, yielding camphorylthiocarbimide and methyl mercaptan:

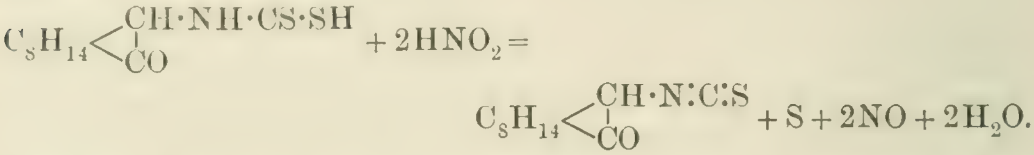


$$C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot CS\cdot S\cdot CH_3\\ CO\end{array} = C_8H_{14}<\begin{array}{l}CH\cdot N{:}C{:}S\\ CO\end{array} + CH_3\cdot SH.$$

We conclude therefore that the stability of camphoryldithiocarbamic acid is merely another manifestation of the remarkable influence exerted by the carbonyl radicle upon the functions of a group attached to the neighbouring carbon atom, and in this association the behaviour of other aminoketones towards carbon disulphide might repay investigation.

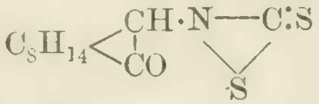
Another interesting distinction from the dithiocarbamic acids, derivatives of which have been described hitherto, is to be found in the power displayed by the camphoryl derivative to yield a benzoyl compound. Numerous alkyl esters of dithiocarbamic acids have been prepared, even from the unstable compounds of the aliphatic and aromatic series, but the action of benzoyl chloride on the acids has either not been studied, or has led to negative results. In the case of phenyldithiocarbamic acid, Busch and Becker, who described definite ethyl and benzyl esters (*J. pr. Chem.*, 1899, [ii], 60, 217), state that the benzoyl derivative cannot be isolated, as it loses water immediately, and gives diphenyl*iso*dithiodiazolone,  $C_6H_5\cdot N<\begin{array}{l}N{—}CS\\ C(C_6H_5)\cdot S\end{array}$, along with *s*-dibenzoylphenylhydrazine. From camphoryldithiocarbamic acid and benzoyl chloride in ether, however, we have obtained a well-defined benzoyl derivative which may be recrystallised; nevertheless, it is easily decomposed into camphorylthiocarbimide and, presumably, thiobenzoic acid, and the mustard oil alone is isolated if the benzoylation of camphoryldithiocarbamic acid is attempted under ordinary conditions in presence of alkali.

The action of nitrous acid on the dithiocarbamic acid, although leading ultimately to the mustard oil, is not quite so simple as would appear from the equation:

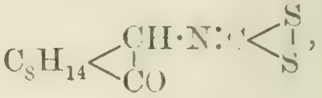


$$C_8H_{14}\Big<\begin{matrix}CH\cdot NH\cdot CS\cdot SH\\ |\\ CO\end{matrix} + 2HNO_2 = C_8H_{14}\Big<\begin{matrix}CH\cdot N{:}C{:}S\\ |\\ CO\end{matrix} + S + 2NO + 2H_2O.$$

There is evidence that an intermediate product of oxidation is first formed without loss of sulphur, because an ethereal solution of camphoryldithiocarbamic acid, when mixed with amyl nitrite, develops a dark brown coloration, and deposits colourless prisms consisting of the substance:



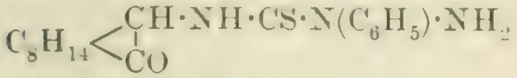
or



unmixed with sulphur; the product may be recrystallised from cold solvents, but, if the temperature is raised, breaks up into camphorylthiocarbimide and sulphur. It may be noted as a curious point that, whilst the specific rotatory power of the oxidation product is $[\alpha]_D$ 102°, the thiocarbimide is lævorotatory, having $[\alpha]_D$ − 114°.

The investigation of camphoryldithiocarbamic acid has brought to light a variety of methods by which the mustard oil may be obtained from it. Two of these have already been mentioned, and a third is the normal decomposition of the mercuric salt when warmed with alcoholic ammonia; a less usual one consists in mixing pyridine solutions of the dithiocarbamic acid and benzoyl chloride, and in attempting to prepare the benzenesulphonic derivative it was found that the thiocarbimide is produced almost quantitatively when an alkaline solution of the dithiocarbamate is agitated with benzenesulphonic chloride. A sixth process depends on the behaviour of camphorylthiocarbamide towards nitrous acid, which does not give rise to a nitroso-derivative, thus classifying the thiocarbamide with camphorylcarbamide instead of with the pseudo-modification.

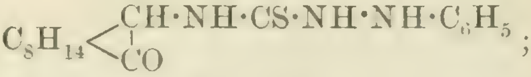
It does not appear probable that the mustard oil will prove serviceable in the task of resolving racemic alcohols, its reaction with the hydroxyl group being sluggish; methyl camphorylthiocarbamate was obtained when the factors were heated at 150° during five hours. The behaviour of the thiocarbimide towards phenylhydrazine is interesting, however, and three definite products have been isolated, two of which have the empirical formula of a camphorylphenylthiosemicarbazide, whilst the third is evidently an internal anhydride or phenylhydrazone. The work of A. E. Dixon (Trans., 1892, **61**, 1012) and of Marckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) has shown that many of the thiosemicarbazides produced from aromatic thiocarbimides and hydrazines exist in two modifications, which Busch and Holzmann (*Ber.*, 1901, **34**, 320) have proved to be structurally distinct (compare also Busch, Opfermann, and Walther, *Ber.*, 1904, **37**, 2318). Owing to lack of material, our examination of the camphorylphenylthiosemicarbazides has not been so complete as that of the authors mentioned, but we believe them to be α- and β-derivatives of phenylhydrazine respectively, as represented by the formulæ:



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot N(C_6H_5)\cdot NH_2\\ |\\ CO\end{matrix}$$

and

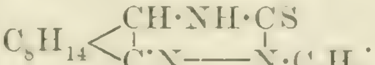
M. p. 183°.



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot NH\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix};$$

M. p. 163°.

the modification melting at 183° readily passes into the anhydride, which most probably has the constitution:

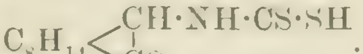


$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\\ |\qquad\qquad |\\ C:N\text{——}N\cdot C_6H_5\end{matrix}.$$

Although the two thiosemicarbazides have almost the same specific rotatory power, the colours which they develop with sulphuric acid, copper acetate, ferric chloride, bleaching powder, nickel acetate, and ammoniacal silver oxide render it a simple matter to distinguish between the isomeric forms, and to differentiate these from the anhydride. We have not been able to transform the α-derivative into the isomeride by boiling the alcoholic solution with a small quantity of hydrochloric acid (compare Marckwald, *loc. cit.*), because this treatment gives rise to the anhydride, but we have shown that, under the same conditions, the β-modification is not converted into the less fusible form.

EXPERIMENTAL.

Camphoryldithiocarbamic Acid,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot SH\\ |\\ CO\end{matrix}.$$

One hundred grams of *iso*nitrosocamphor were reduced in alkaline solution with zinc dust, and the aminocamphor, after extraction with ether, was converted into the hydrochloride and reprecipitated by alkali; the solution in ether was then dried with solid potassium hydroxide, immersed in cold water, and slowly mixed with 48 grams of carbon disulphide. Heat was developed, and when action was complete the solvent was evaporated until about 200 c.c. of liquid remained; as this product cooled, it solidified to a crystalline cake which, when drained on earthenware, weighed 110 grams instead of 134. The substance was recrystallised from methyl alcohol, forming glistening, hexagonal plates which melt and decompose at 128°:

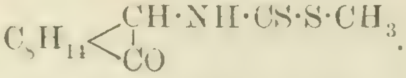
0·2337 gave 12·1 c.c. of nitrogen at 18° and 755·5 mm. N = 5·94.
0·1003 „ 0·1939 $BaSO_4$. S = 26·50.
$C_{11}H_{17}ONS_2$ requires N = 5·77; S = 26·33 per cent.

The yield of dithiocarbamic acid is not impaired when the ethereal solution of aminocamphor is heated with carbon disulphide in a reflux apparatus during many hours, but, if solvents of higher boiling point are used, hydrogen sulphide is liberated slowly, and the normal change into disubstituted thiocarbamide takes place. In recrystallising the substance, therefore, it is advisable to proceed as rapidly as possible, and to deal with moderate quantities; although cold chloroform dissolves it sparingly, an attempt to recrystallise 50 grams from this medium failed, owing to the necessity of boiling it with the solid for some minutes, the filtered liquid depositing no crystals on cooling, and yielding a gummy residue from which dicamphorylthiocarbamide alone was obtainable. Cold acetone or ether and hot methyl and ethyl alcohols dissolve the dithiocarbamic acid freely, forming supersaturated solutions; hot benzene dissolves it sparingly, and it is practically insoluble in boiling light petroleum. The substance is a pronounced acid, dissolving in sodium carbonate and cold dilute caustic alkalis without change, but hot alkalis transform it into dicamphorylthiocarbamide.

A solution containing 0·2614 gram in 25 c.c. of acetone gave a_D 0°27′ in a 2-dcm. tube, whence $[a]_D$ 21·5°; on exposing this liquid to light during several days, it became yellow and lævorotatory to the extent of a_D 0°45′, indicating transformation into camphorylthiocarbimide (see below). A 2 per cent. solution of the dithiocarbamic acid in potassium hydroxide is inactive, and remains so when heated at 90° during several days, when the pale yellow liquid gradually becomes green without depositing dicamphorylthiocarbamide, although this is precipitated on acidification. An alcoholic solution giving a_D 18′ when freshly prepared increased in optical activity to a_D 1°0′ after three months, sulphur separating in well-defined crystals. An ethereal solution of the acid develops a deep brown coloration with ferric chloride, but there is no change when sodium nitroprusside is added to a solution in alcohol or dilute ammonia.

Behaviour towards Metallic Salts.—When alcoholic copper acetate is added to a moderately concentrated solution of camphoryldithiocarbamic acid in the same solvent, a deep brown coloration is developed but there is no precipitate until copper is in excess, when a pale brown derivative appears; on warming this compound in the liquid, it becomes faintly yellow and highly insoluble. Alcoholic silver nitrate develops a deep yellow colour, the liquid remaining clear, but on adding a few drops of alcoholic ammonia a pale brown precipitate is formed, sparingly soluble in boiling alcohol; excess of alcoholic ammonia dissolves this material, and the solution may be boiled without precipitating silver sulphide. Lead acetate forms a bulky, pale yellow salt, which, when boiled with alcohol, deposits lead sulphide in the form of a mirror. A solution of mercuric chloride in alcohol yields a bulky, snow-white precipitate which does not change in appearance when the liquid is boiled. If the solution of camphoryldithiocarbamic acid is faintly ammoniacal, however, the precipitate with alcoholic mercuric chloride is yellow, and quickly becomes black on boiling, whilst the filtered liquid yields crystals of camphorylthiocarbimide.

Methyl Camphoryldithiocarbamate,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot S\cdot CH_3\\ |\\ CO\end{matrix}.$$

Camphoryldithiocarbamic acid combines with methyl iodide very readily, hydrogen iodide being eliminated when the two materials are warmed together. Twenty grams of the acid were dissolved in absolute methyl alcohol containing 2 grams of sodium, and treated with 15 grams of methyl iodide; the deep yellow colour faded, and, after a few minutes on the steam-bath, water was added, the crystalline precipitate being then filtered quickly and washed with cold water. While the substance remained moist, it retained the offensive odour of methyl mercaptan, but this was gradually lost in the desiccator, and on recrystallising the dry material from boiling petroleum, in which it dissolves readily, silky, centimetre-long needles were obtained quite odourless, and melting at 147° without evolving gas:

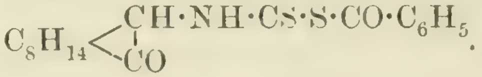
0·2005 gave 9·6 c.c. of nitrogen at 16° and 765 mm. N = 5·62.
0·0957 ,, 0·1730 $BaSO_4$. S = 24·78
$C_{12}H_{19}ONS_2$ requires N = 5·45; S = 24·90 per cent.

A solution containing 1·0450 grams in 25 c.c. of chloroform gave α_D 9° 35′ in a 2-dcm. tube, whence $[\alpha]_D$ 114·6°. The ester is freely soluble in chloroform, benzene, acetone, ether, or ethyl acetate, less readily in methyl and ethyl alcohols; it is very sparingly soluble in cold petroleum, and an ethereal solution gives no colour with ferric chloride.

Decomposition by Heat.—When warmed with water, the odour of methyl mercaptan quickly becomes perceptible, followed by the pungent vapour of camphorylthiocarbimide rising with the steam.

Five grams of the dry ester were mixed with clean, white sand in a small distilling flask connected with a double U-tube immersed in a freezing mixture, the apparatus having been carefully dried, and closed by a tube of calcium chloride. The flask was heated in an oil-bath at 170° during two hours, when approximately 1 c.c. of methyl mercaptan collected in the receiver; this product was identified by conversion into the mercury compound, which melted at 177° after crystallisation from alcohol. The residue in the flask was recognised as camphorylthiocarbimide.

Benzoyl Derivative of Camphoryldithiocarbamic Acid,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot S\cdot CO\cdot C_6H_5\\ |\\ CO\end{matrix}.$$

On attempting to benzoylate camphoryldithiocarbamic acid under the familiar conditions of the Schotten-Baumann process, it was found that camphorylthiocarbimide is the main product. Experiments in which benzoyl chloride acted on the acid dissolved in pyridine gave distinct evidence of the formation of a benzoyl derivative, for, on dissolving the well-washed product in alcohol, ethyl benzoate was recognisable in the liquid, although it was the thiocarbimide which crystallised on cooling. Even when the material arising by benzoylation in pyridine is dried as quickly as possible without heating, and recrystallised from petroleum to exclude water, the benzoyl derivative is mixed with camphorylthiocarbimide, but an individual substance may be obtained by employing ether as a medium.

Ten grams of camphoryldithiocarbamic acid were dissolved in 100 c.c. of dried ether and mixed with 6 grams of benzoyl chloride; on evaporating the solvent in a current of dry air, clusters of yellow needles separated, and on recrystallisation from warm petroleum, in which it is moderately soluble, the benzoyl derivative was obtained in long, colourless, silky needles melting at 105°:

0·2690 gave 9·2 c.c. of nitrogen at 20° and 762·5 mm. N = 3·92.
0·0994 ,, 0·1357 $BaSO_4$. S = 18·74.
$C_{18}H_{21}O_2NS_2$ requires N = 4·03; S = 18·44 per cent.

A solution containing 0·2865 gram in 25 c.c. of chloroform gave α_D 1°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 52·3°. The benzoyl derivative is freely soluble in chloroform, benzene, acetone, and ethyl acetate, less readily in methyl and ethyl alcohols, solutions in these media depositing camphorylthiocarbimide on cooling; even when petroleum is employed, there is danger of decomposing the benzoyl derivative, and it is only by operating with small quantities, and cooling the liquid as rapidly as possible, that a specimen of the benzoyl derivative unmixed with thiocarbimide can be obtained.

Action of Amyl Nitrite on Camphoryldithiocarbamic Acid.

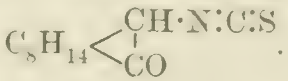
In preparing camphorylthiocarbimide by the action of nitrous acid on camphoryldithiocarbamic acid (see below), various indications suggested the formation of an intermediate compound which passed into the mustard oil with loss of sulphur, and this material was ultimately isolated in the following manner.

Camphoryldithiocarbamic acid was dissolved in dry ether and mixed with an equal weight of amyl nitrite, which immediately developed a dark reddish-brown coloration, followed by continuous evolution of red gas; as the effervescence proceeded, the colour of the liquid gradually disappeared and colourless prisms separated. Attempts to recrystallise this material led at first to the thiocarbimide with elimination of sulphur, but on dissolving the substance in chloroform and adding petroleum, colourless crystals were obtained which become yellow at about 110°, melting and decomposing at 116°:

0·3287 gave 16·4 c.c. of nitrogen at 20° and 755 mm. N = 5·67.
0·0936 ,, 0·1776 $BaSO_4$. S = 26·05.
$C_{11}H_{15}ONS_2$ requires N = 5·81; S = 26·55 per cent.

The formulæ $C_{11}H_{15}ONS_2$ and $C_{22}H_{32}O_2N_2S_4$ being indistinguishable by analysis, determinations of molecular weight were made in benzene and in phenol. In the former solvent, the results were abnormal, averaging about 700, but in phenol an average of 227 was obtained, corresponding with the simpler formula $C_{11}H_{15}ONS_2$, which requires 241, whilst $C_{22}H_{32}O_2N_2S_4$ amounts to 484. A solution containing 0·3072 gram in 25 c.c. of chloroform gave α_D 2°30′ in a 2-dcm. tube, whence $[\alpha]_D$ 101·7°. The substance is freely soluble in chloroform or benzene, but dissolves less readily in acetone or ethyl acetate; methyl and ethyl alcohols dissolve it sparingly, and it is practically insoluble in light petroleum.

Camphorylthiocarbimide (Camphoryl Mustard Oil),



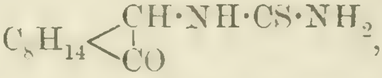
$$C_8H_{14}<\begin{matrix}CH\cdot N:C:S\\ |\\ CO\end{matrix}.$$

Twenty grams of camphoryldithiocarbamic acid were dissolved in 50 c.c. of pyridine, cooled with ice, and mixed with 12 grams of benzoyl chloride, also dissolved in pyridine; the temperature rose, and pyridine hydrochloride separated. After ten minutes, ice-water was added, the oily precipitate quickly becoming solid; this was drained on earthenware and boiled with alcohol containing a small proportion of water, the hot liquid depositing 17 grams of thiocarbimide as it cooled. The following alternative method was also satisfactory.

Twenty c.c. of concentrated hydrochloric acid were added to 10 grams of camphoryldithiocarbamic acid dissolved in 200 c.c. of absolute alcohol, the ice-cold liquid being then treated with 5 grams of sodium nitrite in the minimum quantity of water. The first portions of the salt developed an intense brown coloration in the liquid, and a colourless precipitate was formed; this was collected after two hours, digested with warm absolute alcohol, and the solution filtered from sulphur and sodium chloride. On adding water, the thiocarbimide was precipitated, and, when recrystallised from a small quantity of hot absolute alcohol, separated in long, lustrous prisms which melt at 106·5°:

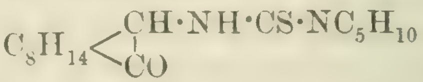
0·1804 gave 10·4 c.c. of nitrogen at 20° and 771·5 mm. N = 6·70.
0·1068 ,, 0·1174 $BaSO_4$. S = 15·07.
$C_{11}H_{15}ONS$ requires N = 6·70; S = 15·31 per cent.

A solution containing 0·2263 gram in 25 c.c. of absolute alcohol gave α_D −2°4′ in a 2-dcm. tube, whence $[\alpha]_D$ −114·1°; after several weeks, the activity of the solution almost disappeared, becoming stationary at α_D −0°5′. The mustard oil is readily soluble in benzene, and moderately so in alcohol; petroleum dissolves it readily when boiled, depositing lustrous, silky needles on cooling. It is insoluble in water, and the vapour in steam has a pungent odour which recalls that of camphorylcarbimide rather than phenyl mustard oil; boiling water and alkalis convert it slowly into dicamphorylthiocarbamide. Although sluggish in its action on water and alcohols, it reacts readily with ammonia and amines, yielding the following typical derivatives.

Camphorylthiocarbamide,  $C_8H_{14}{<}\begin{array}{l}CH\cdot NH\cdot CS\cdot NH_2\\ \mid\\ CO\end{array}$, prepared by passing dry ammonia into a solution of the thiocarbimide in chloroform, separated on adding petroleum as an oil which rapidly solidified; when recrystallised from boiling water, it formed slender laminæ with silky lustre, and melted at 180°, evolving gas:

0·2078 gave 22·1 c.c. of nitrogen at 15·5° and 764 mm. N = 12·49.
$C_{11}H_{18}ON_2S$ requires N = 12·41 per cent.

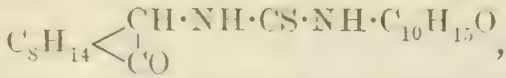
A solution containing 0·2640 gram in 25 c.c. of chloroform gave α_D −0°57′ in a 2-dcm. tube, whence $[\alpha]_D$ −44·9°. The substance dissolves readily in cold alcohol, and is moderately soluble in boiling water and in hot benzene, but is practically insoluble in petroleum. With nitrous acid, it gives the thiocarbimide, behaving in this respect like camphorylcarbamide (Trans., 1905, **87**, 118).

Camphorylpiperidylthiocarbamide,  $C_8H_{14}{<}\begin{array}{l}CH\cdot NH\cdot CS\cdot NC_5H_{10}\\ \mid\\ CO\end{array}$, was produced when the thiocarbimide, dissolved in a small proportion of benzene, was mixed with piperidine; heat was developed, and, after an interval, petroleum was added, the precipitated piperidyl derivative being then dissolved in dilute hydrochloric acid, filtered from a small quantity of dicamphorylthiocarbamide, and again precipitated with potassium hydroxide. Recrystallisation from alcohol gave well-formed, rhombic prisms melting at 188°:

0·1047 gave 0·0853 $BaSO_4$. S = 11·17.

$C_{16}H_{26}ON_2S$ requires S = 10·88 per cent.

A solution containing 0·3130 gram in 25 c.c. of chloroform gave α_D 0°40′ in a 2-dcm. tube, whence $[\alpha]_D$ 26·6°. The substance is freely soluble in chloroform or pyridine, readily in benzene or acetone, and moderately in methyl alcohol or ethyl acetate, from which it crystallises in transparent prisms; boiling petroleum dissolves it sparingly, however, and it separates from this medium in lustrous, silky needles.

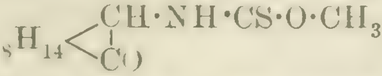
Dicamphorylthiocarbamide,  $C_8H_{14}{<}\begin{matrix}CH\cdot NH\cdot CS\cdot NH\cdot C_{10}H_{15}O\\ |\\ CO\end{matrix}$, is obtained by the action of water, acids, and alkalis on the thiocarbimide, and crystallises from alcohol in colourless, glistening plates resembling thiocarbanilide; it melts at 176°:

0·2050 gave 12·75 c.c. of nitrogen at 16·5° and 780 mm. N = 7·43.
0·1050 ,, 0·0639 $BaSO_4$. S = 8·34.

$C_{21}H_{32}O_2N_2S$ requires N = 7·44; S = 8·51 per cent.

A solution containing 0·4832 gram in 25 c.c. of acetone gave α_D 2°6′ in a 2-dcm. tube, whence $[\alpha]_D$ 54·3°. The substance is readily soluble in chloroform, acetone, or glacial acetic acid, but only moderately in ether, ethyl acetate, methyl alcohol, or benzene; it is insoluble in cold petroleum, but dissolves very sparingly on boiling. When ethereal ferric chloride is added to a solution of the thiocarbamide in ether, no change is noticeable at first, but a pale brown, flocculent precipitate separates in the course of a few minutes.

Unlike thiocarbanilide, dicamphorylthiocarbamide is insoluble in alkalis; it is also insoluble in dilute acids, and resists the action of concentrated hydrochloric acid. It appears to be capable of undergoing transformation into a pseudo-modification, because a solution of camphoryldithiocarbamic acid in excess of potassium hydroxide remains clear when heated at 90° during several hours, although dicamphorylthiocarbamide is insoluble in potassium hydrogen sulphide.

Methyl camphorylthiocarbamate,  ${}_8H_{14}{<}\begin{matrix}CH\cdot NH\cdot CS\cdot O\cdot CH_3\\ |\\ CO\end{matrix}$, is formed when the mustard oil is heated in a sealed tube during five hours at about 150° with absolute methyl alcohol; it displays a tendency to form supersaturated solutions in methyl alcohol, but may be conveniently recrystallised from petroleum, when it melts at 118°:

0·2268 gave 11·7 c.c of nitrogen at 17° and 764 mm. $N = 6·02$.
$C_{12}H_{19}O_2NS$ requires $N = 5·81$ per cent.

A solution containing 0·3645 gram in 25 c.c. of chloroform gave α_D 3°10′ in a 2-dcm. tube, whence $[\alpha]_D$ 108·6°. The substance is freely soluble in methyl and ethyl alcohols, chloroform, benzene, or ethyl acetate.

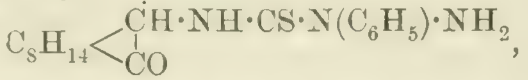
The Camphorylphenylthiosemicarbazides.

Camphorylthiocarbimide and phenylhydrazine interact very readily when brought together in moderately dilute solutions. A great number of experiments have been made with the object of determining the conditions favouring the production of each modification, but the two thiosemicarbazides appear to be formed simultaneously, and require to be separated by fractional crystallisation. The following two experiments are typical of many.

Eight grams of the thiocarbimide were dissolved in chloroform and treated with 5 grams of phenylhydrazine. When the solvent had evaporated spontaneously, the gummy residue was warmed with methyl alcohol, which caused crystals to separate on cooling; this product, weighing about 6 grams, was recrystallised from methyl alcohol, separating in thin, lustrous plates melting at 183°. The mother-liquors yielded a small proportion of the anhydride, melting at 235°, along with about 4 grams of needles, more freely soluble in methyl alcohol, and melting at 163°.

Nine grams of the thiocarbimide dissolved in 120 c.c. of ether, to which a small quantity of alcohol had been added, were cooled in ice, and treated with 6 grams of phenylhydrazine, also dissolved in ether; the liquid changed to a clear, tough jelly, which underwent but slight shrinkage during six hours. This was dissolved in 20—30 c.c. of hot alcohol and warmed until the ether was removed; 8 grams of the less fusible thiosemicarbazide were deposited from this solution, the mother-liquor yielding about 1 gram of the isomeride.

The *camphorylphenylthiosemicarbazide*,



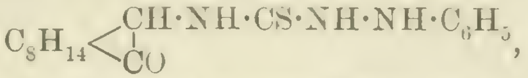
$$C_8H_{14}<\begin{matrix}\dot{C}H\cdot NH\cdot CS\cdot N(C_6H_5)\cdot NH_2\\ |\\ CO\end{matrix},$$

which melts at 183°, is obtained with comparative ease, owing to its relatively sparing solubility, but it has the inconvenient property of yielding a tough, transparent jelly when dissolved in ether, alcohol, or petroleum, a peculiarity which has been recently noticed by E. Fischer and Abderhalden (*Ber.*, 1907, **40**, 3558) in connexion with a substance, $C_7H_{12}O_2N_2$, obtained from elastin by hydrolysis. We have made experiments to ascertain the minimum of material which is capable of producing this jelly, and find that if the thiosemicarbazide is first dissolved in a small quantity of hot alcohol, and the solution diluted with petroleum, one part in 300 gives a tough, transparent jelly, which does not liquefy during twenty-four hours; after this period, however, the medium gradually becomes limpid, and the solid separates in well-defined crystals, which at first appear suspended in the jelly:

0·1986 gave 23·1 c.c. of nitrogen at 19° and 759 mm. N = 13·35.
0·1847 „ 0·1325 $BaSO_4$. S = 9·85.
$C_{17}H_{23}ON_3S$ requires N = 13·25; S = 10·09 per cent.

A solution containing 0·3153 gram in 25 c.c. of chloroform gave α_D 1°31′ in a 2-dcm. tube, whence $[\alpha]_D$ 59·5°. The substance is insoluble in aqueous alkali, and is readily converted into the anhydride, described below, when the alcoholic solution is heated with a small quantity of hydrochloric acid, or when an attempt is made to recrystallise the solid from glacial acetic acid. An estimation of the molecular weight in benzene gave an average of 338 units, the value calculated from the empirical formula $C_{17}H_{23}ON_3S$ being 317.

The *camphorylphenylthiosemicarbazide*,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot NH\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix},$$

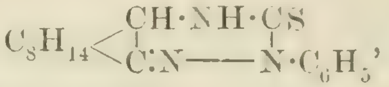
which melts at 163°, is produced in small quantities only, even under the most favourable conditions:

0·2270 gave 25·5 c.c. of nitrogen at 22° and 765 mm. N = 12·82.
0·1016 „ 0·0767 $BaSO_4$. S = 10·36.
$C_{17}H_{23}ON_3S$ requires N = 13·25; S = 10·09 per cent.

A solution containing 0·2134 gram in 25 c.c. of chloroform gave α_D 1°0′ in a 2-dcm. tube, whence $[\alpha]_D$ 58·5°. Although the degree of optical activity is almost identical with that of the isomeric substance, the following colour tests serve to distinguish between the two materials; to render the comparison more convenient, the various reactions are tabulated alongside with those of the anhydride:

	M. p. 163°.	M. p. 183°.	Anhydride.
Concentrated sulphuric acid.	Rich blue.	Deep yellow.	Colourless.
Alcoholic copper acetate.	Intense bluish-green.	Intense, but transient, brown.	Transient brown, less intense.
Alcoholic copper nitrate.	Intense blue.	Blue, less intense.	Grass-green.
Alcoholic nickel acetate.	Colourless at first, purple on warming.	Grass-green.	No change.
Ethereal ferric chloride.	No change.	Deep red.	No change.

	M. p. 163°.	M. p. 183°.	Anhydride.
Alcoholic silver nitrate.	White opalescence, pale brown on boiling.	White opalescence, black on boiling.	No change, even on boiling.
Ammoniacal silver oxide.	Yellow coloration, becoming green; black precipitate on boiling.	White opalescence, intensifying to a brown precipitate on boiling.	Immediate yellow precipitate, which does not darken on boiling.
Bleaching powder solution.	Deep orange.	Pale yellow.	No change.

The *anhydride*,  $C_8H_{14}<\begin{matrix} CH\cdot NH\cdot CS \\ | \qquad\quad | \\ C:N \text{——} N\cdot C_6H_5 \end{matrix}$, crystallises in small, lustrous needles melting at 235°:

0·2153 gave 26·8 c.c. of nitrogen at 20° and 762 mm. N = 14·28.
0·1007 „ 0·0783 $BaSO_4$. S = 10·68.

$C_{17}H_{21}N_3S$ requires N = 14·04; S = 10·70 per cent.

A solution containing 0·2823 gram in 25 c.c. of chloroform gave α_D 6°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 274·5°. The substance is sparingly soluble in methyl and ethyl alcohols, ethyl acetate, or benzene, more readily, however, in acetone and chloroform; it is freely soluble in pyridine, but practically insoluble in petroleum.

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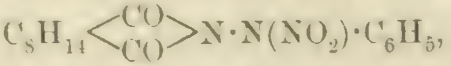
CLXXXIII.—*Aromatic Amides and Imides of Camphoric Acid.*

By William Ord Wootton.

The derivatives of camphoric acid described in this communication were prepared with the object of obtaining an amino-compound, which, while displaying the stability and reactivity of an aromatic amine, should at the same time exhibit the optical properties usually associated with the presence of a camphor nucleus. It was thought that such a compound might prove useful in the study of certain racemic aldehydes, the resolution of which the author desires to effect.

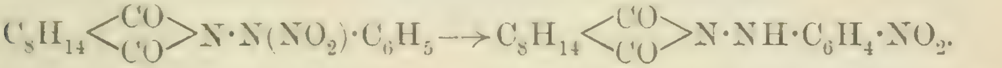
Since camphorylphenylhydrazide, an optically active and readily accessible substance, might be supposed to yield nitro-derivatives, and consequently aromatic amines, the action of nitric acid on this compound was first studied. It was found that the products of nitration were more complex than was at first supposed, the action of nitric acid (sp. gr. 1·42) leading to the formation of a mixture of substances from which a new nitroamine, N-*nitrocamphorylphenylhydrazide*,



$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot N(NO_2)\cdot C_6H_5,$$

was isolated. It was incidentally discovered that the substance obtained by the action of nitrous acid on camphorylphenylhydrazide is N-*nitrosocamphorylphenylhydrazide*, and not a nitro-compound as stated by E. M. Chaplin (*Ber.*, 1892, **25**, 2565). Similar pairs of *N*-nitro- and *N*-nitroso-compounds have been obtained from two new bromo-derivatives of camphorylphenylhydrazide.

The *N*-nitro-compounds appear to exhibit the property, characteristic of nitroamines in the aromatic series, of passing readily into isomeric *C*-nitro-compounds. Thus, when boiled with solvents or simply heated to fusion, the nitro-group migrates from the aminic group to one of the carbon atoms in the benzene nucleus :



$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot N(NO_2)\cdot C_6H_5 \longrightarrow C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot NH\cdot C_6H_4\cdot NO_2.$$

A mixture of isomeric *C*-nitro-compounds is probably produced, and it is intended to continue the study of this transformation.

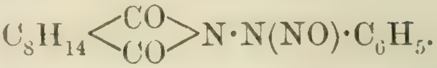
The nitroso-derivatives in this series are very pale yellow, the corresponding *N*-nitro-derivatives are colourless, whilst the *C*-nitro-compounds have a yellow colour. The nitroso-compounds become colourless when cooled to the temperature of liquid air.

The complexity of this nitration has up to the present precluded the possibility of obtaining an aromatic amino-derivative of camphorylphenylhydrazide in a state of purity. It has been found, however, that, by condensing together camphoric anhydride and *p*-bromoaniline, an anilide is obtained ; this, on nitration and subsequent reduction, yields a well-defined amino-compound which, in alcoholic solution, shows $[\alpha]_D$ 49·7°. The behaviour of this base towards aldehydes will be described in a further communication.

Attempts to prepare 4-amino- and 3-amino-phenyl-α-camphoramic acids through the condensation of camphoric anhydride with the *p*- and *m*-nitroanilines respectively were unsuccessful, owing to the difficulty with which these substances react. The 4-amino-compound was, however, ultimately obtained by the reduction of 4-*benzeneazophenyl-α-camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_5$, a substance which is interesting as being one of the few recorded instances of optically active aromatic azo-compounds.

EXPERIMENTAL.

N-*Nitrosocamphorylphenylhydrazide*,



$$C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot N(NO)\cdot C_6H_5.$$

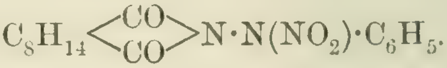
This substance is most conveniently prepared by treating camphorylphenylhydrazide dissolved in glacial acetic acid with the requisite quantity of sodium nitrite in 20 per cent. aqueous solution. The compound is precipitated by the addition of water and recrystallised from alcohol, from which it separates in yellow needles melting without decomposition at 157°. Repeated crystallisation from various solvents failed to remove the colour of the substance. A specimen prepared by Chaplin's method was found to melt at 157°, and not to depress the melting point of the preceding preparation:

0·1179 gave 0·2722 CO_2 and 0·0663 H_2O. C = 62·97; H = 6·25.
0·1014 ,, 0·2369 CO_2 and 0·0531 H_2O. C = 63·69; H = 5·82.
0·2318 ,, 27·6 c.c. nitrogen at 15° and 755 mm. N = 13·85.
$C_{16}H_{19}O_3N_3$ requires C = 63·79; H = 6·31; N = 13·95 per cent.

0·4330 in 25 c.c. of chloroform in a 2-dcm. tube gave α_D 0·49°, whence $[\alpha]_D$ 14·1°.

This nitroso-compound gives the Liebermann reaction with intense colorations in all its phases. Reduction with aluminium amalgam in moist ethereal solution leads to the formation of camphorylphenylhydrazide and ammonia.

N-*Nitrocamphorylphenylhydrazide*,



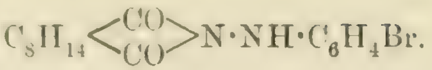
$$C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot N(NO_2)\cdot C_6H_5.$$

This was prepared by dissolving 10 grams of camphorylphenylhydrazide in 20 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride. The solution was cooled in ice and treated with a mixture of 2 c.c. of nitric acid (sp. gr. 1·5) and 2 c.c. of acetic anhydride. After thirty minutes, the nitro-compound was precipitated by the cautious addition of water. By recrystallisation from carbon disulphide or chloroform, in which the compound is very soluble, it was obtained in large, colourless prisms melting at 115—116° to a deep red liquid. The compound is soluble in alcohol or in glacial acetic acid, but if boiled with these solvents decomposition takes place:

0·0888 gave 0·1978 CO_2 and 0·0463 H_2O. C = 60·75; H = 5·80.
$C_{16}H_{19}O_4N_3$ requires C = 60·56; H = 5·99 per cent.

0·3594 in 20 c.c. of chloroform in a 2-dcm. tube gave α_D 0·58°, whence $[\alpha]_D$ 16·1°.

The fact that camphorylphenylhydrazide and ammonia are produced when this compound is reduced indicates that the nitro-group is not attached to one of the carbon atoms in the benzene nucleus.

Camphoryl-4-bromophenylhydrazide,  $C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot NH\cdot C_6H_4Br$.

This derivative was obtained, in the first instance, by treating camphorylphenylhydrazide (1 mol.) in glacial acetic acid solution with bromine (1 mol.). The product did not attain a constant melting point until it had been crystallised four times from glacial acetic acid and five times from alcohol, when it was obtained in colourless, lath-like crystals melting at 182—183°. It would appear that a small quantity of an isomeride is produced in this bromination, probably 2-bromocamphorylphenylhydrazide :

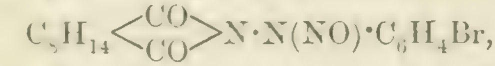
0·2492 gave 17 c.c. of nitrogen at 20° and 762 mm. N = 7·83.
0·2168 ,, 0·1300 AgBr. Br = 22·42.
$C_{16}H_{19}O_2N_2Br$ requires N = 7·98 ; Br = 22·79 per cent.

0·2454 in 20 c.c. of absolute alcohol in a 2-dcm. tube gave α_D 0·66°, whence $[\alpha]_D$ 26·9°.

When boiled for some hours with 10 per cent. aqueous potassium hydroxide, potassium camphorate, phenol, bromobenzene, and ammonia are produced.

The orientation of the bromine atom was accomplished by condensing camphoric anhydride with *p*-bromophenylhydrazine. When these were heated together in molecular proportions at 130—150°, a vigorous action ensued. The brown, glassy mass obtained on cooling was recrystallised from alcohol, when colourless needles, melting at 182—183°, were obtained which were identical with the product of the foregoing bromination, inasmuch as they did not depress the melting point of the first preparation.

N-Nitrosocamphoryl-4-bromophenylhydrazide,



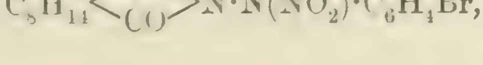
$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot N(NO)\cdot C_6H_4Br,$$

separated as a crystalline precipitate when sodium nitrite in aqueous solution was added to a glacial acetic acid solution of camphoryl-4-bromophenylhydrazide. When recrystallised successively from alcohol and carbon disulphide, it formed fine, pale yellow needles melting without decomposition at 154—155° :

0·1135 gave 0·2100 CO_2 and 0·0506 H_2O. C = 50·46 ; H = 4·95.
0·2110 ,, 20·7 c.c. of nitrogen at 16° and 756 mm. N = 11·36.
$C_{16}H_{18}O_3N_3Br$ requires C = 50·53 ; H = 4·71 ; N = 11·05 per cent.

0·3868 in 20 c.c. of chloroform in a 2-dcm. tube gave α_D 0·70°, whence $[\alpha]_D$ 18·1°.

N-Nitrocamphoryl-4-bromophenylhydrazide,



$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot N(NO_2)\cdot C_6H_4Br,$$

was formed when a mixture of acetic anhydride and nitric acid (sp. gr. 1·5) was slowly added to a solution of camphoryl-4-bromophenylhydrazide in glacial acetic acid. The white, crystalline precipitate was washed successively with glacial acetic acid, acetone, and ether; it was thus obtained in the pure state and quite colourless. It is only sparingly soluble in the usual organic solvents:

0·1069 gave 0·1923 CO_2 and 0·0462 H_2O. C = 49·05; H = 4·80.
0·2283 ,, 21·0 c.c. of nitrogen at 16° and 755 mm. N = 10·65.
$C_{16}H_{18}O_4N_3Br$ requires C = 48·48; H = 4·55; N = 10·60 per cent.

0·3432 in 20 c.c. of chloroform in a 2-dcm. tube gave α_D 0·48°, whence $[\alpha]_D$ 14·0°.

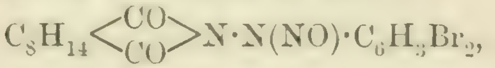
When slowly heated, this compound becomes yellow at about 130°, and on further heating melts very indefinitely. If, however, the substance contained in a capillary tube is placed in a bath at 155°, it melts sharply to a dark red liquid at 159—160°. The original nitro-derivative is only sparingly soluble in alcoholic potash, giving a colourless solution; after fusion, however, the product is freely soluble in this reagent, the solution being blood-red at first, but becoming purple when diluted with water and allowed to remain for several hours. When the *N*-nitro-compound is boiled for a few minutes with glacial acetic acid, it passes into solution, the liquid gradually becoming yellow. The addition of water occasions the formation of a yellow precipitate, from which, however, no definite crystallisable substance has yet been isolated. Like the product of fusion, this precipitate is readily soluble in alcoholic potash to a deep red solution; unlike the original *N*-nitro-compound, it is freely soluble in the usual organic solvents. These facts are explicable on the supposition that through the action of heat the nitro-group has wandered from the amino-group to the benzene nucleus, where its proximity to the aminic hydrogen atom has conferred sufficient acidity on the compound to enable it to form soluble salts when treated with potassium or sodium hydroxide. This is confirmed by the behaviour of the yellow substance on reduction, when an almost colourless basic product is obtained. This can be diazotised; the diazo-solution gives a red coloration when added to alkaline β-naphthol, thus indicating the formation of an azo-compound.

The *N*-nitro-derivative on reduction yields camphoryl-4-bromophenylhydrazide and ammonia.

Camphoryldibromophenylhydrazide, $C_8H_{14}{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}N\cdot NH\cdot C_6H_3Br_2$.—Camphorylphenylhydrazide (1 mol.) was dissolved in glacial acetic acid and treated with bromine (2 mols.). After twelve hours, the greater part of the dibromo-derivative had separated in glistening needles. When recrystallised from glacial acetic acid, it melted at 198—199°:

0·3229 gave 18·1 c.c. of nitrogen at 17° and 765 mm. N = 6·47.
0·2649 „ 0·2299 AgBr. Br = 36·93.
$C_{16}H_{18}O_2N_2Br_2$ requires N = 6·51; Br = 37·21 per cent.

N-*Nitrosocamphoryldibromophenylhydrazide*,



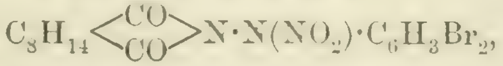
$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot N(NO)\cdot C_6H_3Br_2,$$

separated from hot alcohol in small, heavy, pale yellow, rhombic prisms melting at 147—148°:

0·2502 gave 19·8 c.c. of nitrogen at 15° and 755 mm. N = 9·20.
0·2287 „ 0·1870 AgBr. Br = 34·79.
$C_{16}H_{17}O_3N_3Br_2$ requires N = 9·15; Br = 34·85 per cent.

0·2776 in 15 c.c. of chloroform in a 2-dcm. tube gave α_D 0·70°, whence $[\alpha]_D$ 19·0°.

N-*Nitrocamphoryldibromophenylhydrazide*,



$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot N(NO_2)\cdot C_6H_3Br_2,$$

prepared in a similar manner to the corresponding monobromo-derivative, crystallised from a mixture of acetone and alcohol in glistening, colourless, rhombic prisms melting at 140—142° with decomposition:

0·2333 gave 0·1834 AgBr. Br = 33·46.
$C_{16}H_{17}O_4N_3Br_2$ requires Br = 33·68 per cent.

0·3142 in 15 c.c. of chloroform in a 2-dcm. tube gave α_D 0·46°, whence $[\alpha]_D$ 10·9°.

Derivatives of α-Camphoramic Acid.

4-*Bromophenyl-α-camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4Br$.

When camphoric anhydride and *p*-bromoaniline are heated together in molecular proportions at 120°, combination takes place with considerable evolution of heat. The molten material rapidly sets to a brittle, crystalline mass, which, when crystallised two or three times from dilute alcohol, forms thin, brilliant prisms melting at 206—207°

0·1534 gave 0·0811 AgBr. Br = 22·51.
$C_{16}H_{20}O_3NBr$ requires Br = 22·60 per cent.

0·6912 in 25 c.c. of absolute alcohol in a 2-dcm. tube gave α_D 2·60°, whence $[\alpha]_D$ 47·0°.

This acid is freely soluble in acetone or alcohol, sparingly so in benzene, and insoluble in water or light petroleum. It is readily soluble in aqueous solutions of alkalis or alkali carbonates.

The *sodium* salt was obtained as a bulky, gelatinous mass, possessing an extremely nauseous taste.

The *silver* salt is sparingly soluble in hot water, from which, on cooling, it separates in minute leaflets.

4-*Bromo-3-nitrophenyl-a-camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_3Br\cdot NO_2$.

To a mixture of 30 c.c. of nitric acid (sp. gr. 1·5) and 24 c.c. of glacial acetic acid are added, in small portions at a time, 10 grams of 4-bromophenyl-a-camphoramic acid. After thirty minutes, the clear solution is poured on to ice, when the nitro-compound separates as a yellow precipitate. After recrystallisation from alcohol, in which it is only moderately soluble, it is obtained in bright yellow, hexagonal plates melting at 204—206°:

0·1900 gave 0·0900 AgBr. Br = 20·16.

$C_{16}H_{19}O_5N_2Br$ requires Br = 20·05 per cent.

0·2996 in 20 c.c. of absolute alcohol in a 2-dcm. tube gave α_D − 1·45°, whence $[\alpha]_D$ − 48·4°.

The *sodium* salt of this acid forms yellow leaflets readily soluble in water. When boiled with sodium hydroxide, it is hydrolysed with formation of sodium camphorate and 4-bromo-3-nitroaniline. The latter substance after recrystallisation was found to melt at 112° (Hübner gives 111°).

4-*Bromo-3-aminophenyl-a-camphoramic acid*,

$CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_3Br\cdot NH_2$,

is most conveniently prepared by dissolving 1 part of the foregoing nitro-acid in excess of aqueous ammonia and adding 4 parts of ferrous sulphate dissolved in water in small portions at a time. When the ferrous hydroxide at first precipitated has completely changed into ferric hydroxide, the mixture is heated on the water-bath for a short time with frequent stirring and then filtered by the aid of the pump. On neutralising the filtrate with acetic acid, the amino-compound separates as a bulky, white precipitate. The yield approximates to 75 per cent. of the theoretical. By recrystallisation from dilute alcohol, the substance is obtained in stellate clusters of colourless needles melting at 207—208°:

0·2194 gave 14·4 c.c. of nitrogen at 20° and 758 mm. N = 7·49.
0·2824 „ 0·1414 AgBr. Br = 21·31.

$C_{16}H_{21}O_3N_2Br$ requires N = 7·59; Br = 21·68 per cent.

0·4878 in 25 c.c. of absolute alcohol in a 2-dcm. tube gave α_D 1·59°, whence $[\alpha]_D$ 40·7°.

This amino-acid is readily soluble in aqueous alkalis and alkali carbonates, but less so in concentrated hydrochloric acid. The *hydrochloride* is obtained as a white, amorphous precipitate by passing hydrogen chloride into a solution of the base in acetone. When submitted to the action of nitrous acid, the hydrochloride appears to yield a colourless, insoluble diazo-anhydride.

The *acetyl* derivative is freely soluble in aqueous alkalis, and separates from dilute alcohol in iridescent leaflets melting at 217—219°.

4-*Benzeneazophenyl-α-camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_5$.

This compound results when equimolecular weights of camphoric anhydride and aminoazobenzene are heated together for a short time at 150—180°. It is separated from unchanged material by extraction with aqueous ammonia, reprecipitated from the ammoniacal solution by the addition of acid, and crystallised several times from alcohol. The compound is thus obtained in beautiful orange-red needles melting at 223—224°:

0·2030 gave 20·0 c.c. of nitrogen at 23° and 760 mm. N = 11·10.
$C_{22}H_{25}O_3N_3$ requires N = 11·08 per cent.

0·1483 in 25 c.c. of absolute alcohol in a 2-dcm. tube gave α_D 1·04°, whence $[\alpha]_D$ 87·7°.

This compound dissolves in concentrated sulphuric acid to a deep yellow solution. The alkali salts are yellow and soluble in water. The *calcium* salt, however, is excessively insoluble; it is precipitated in fine yellow needles when a few drops of hard water are added to a solution of one of the alkali salts. Reduction of an alcoholic solution of the acid by means of stannous chloride results in the formation of aniline and 4-*aminophenyl-α-camphoramic acid*

$$CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2.$$

This somewhat unstable substance was obtained as a white or light grey, amorphous powder, readily soluble in alcohol, acetone, or chloroform, and in solutions of sodium hydroxide or sodium carbonate, but insoluble in water or light petroleum. From solutions, however, it separated in a resinous condition, and became solid only when left for several days; it could not be obtained crystalline:

0·2292 gave 20·4 c.c. of nitrogen at 23° and 752 mm. N = 9·92.
$C_{16}H_{22}O_3N_2$ requires N = 9·66 per cent.

On attempting to acetylate this base, it underwent decomposition. The *acetyl* derivative, however, was ultimately obtained by heating together camphoric anhydride and 4-aminoacetanilide either alone or with a solvent. From dilute acetic acid, the compound crystallises in glistening leaflets melting at 233—234°. An attempt to prepare the foregoing base by the fractional hydrolysis of this acetyl derivative was unsuccessful, only *p*-phenylenediamine and its oxidation products being obtained.

Derivatives of N-Phenylcamphorimide.

The 4-*bromo*-derivative, $C_8H_{14}<\substack{CO\\CO}>N\cdot C_6H_4Br$, is produced when 4-bromophenyl-α-camphoramic acid is heated for an hour with glacial acetic acid and acetic anhydride. Unchanged bromo-acid is removed by extraction with aqueous ammonia. The new imide forms prisms, sparingly soluble in hot alcohol and melting at 180—181°:

0·1939 gave 0·1074 AgBr. Br = 23·57.
$C_{16}H_{18}O_2NBr$ requires Br = 23·80 per cent.

The 4-*bromo*-3-*nitro*-derivative, $C_8H_{14}<\substack{CO\\CO}>N\cdot C_6H_3Br\cdot NO_2$, is readily prepared in quantitative yield when the preceding compound is dissolved in cold nitric acid (sp. gr. 1·5). From hot alcohol, it crystallises in clusters of short, pale yellow needles which melt at 171—172°. When treated with tin and hydrochloric acid in alcoholic solution, reduction to the corresponding amino-compound is effected:

0·1397 gave 8·7 c.c. of nitrogen at 19° and 754 mm. N = 7·10.
$C_{16}H_{17}O_4N_2Br$ requires N = 7·35 per cent.

The 4-*bromo*-3-*amino*-derivative, $C_8H_{14}<\substack{CO\\CO}>N\cdot C_6H_3Br\cdot NH_2$, a somewhat ill-defined base, dissolving freely in alcohol, acetone, or chloroform, is deposited on cooling the warm solutions as a colourless oil which on trituration is converted into a white, microcrystalline solid melting at about 130°:

0·1257 gave 8·6 c.c. of nitrogen at 25° and 762 mm. N = 7·66.
$C_{16}H_{19}O_2N_2Br$ requires N = 7·98 per cent.

A solution of this base in acetone is feebly dextrorotatory.

The *hydrochloride* is decomposed by water; on diazotisation, it forms a clear solution which, when added to alkaline β-naphthol, yields a scarlet azo-compound.

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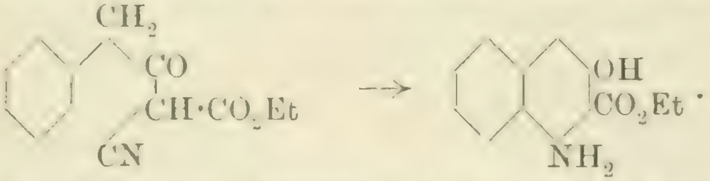
CLXXXIV.—*Ethyl* α-*Cyano*-γ-*phenylacetoacetate.*

By Arthur Richard Smith and Jocelyn Field Thorpe.

After it had been proved that ethyl β-imino-α-cyano-γ-phenylbutyrate passed on treatment with concentrated sulphuric acid into ethyl 1 : 3-naphthylenediamine-2-carboxylate (Trans., 1906, **89**, 1906), it seemed of importance to ascertain the nature of the reaction which would ensue between the corresponding ketone, namely, ethyl α-cyano-γ-phenylacetoacetate, and concentrated sulphuric acid, since it might be expected that in this case ring formation would also take place with the production of ethyl 4-amino-2-naphthol-3-carboxylate, thus :



It was found, however, that although concentrated sulphuric acid instantly acted on the ketone, forming a deep malachite-green solution, yet the products formed appeared to be of high molecular complexity, and no crystalline compound has as yet been isolated from them. There is, however, a great resemblance between these products and those which are formed to so large an extent when ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate and ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate are treated with concentrated sulphuric acid (Trans., 1907, **91**, 1687), and it is hoped that the identification of these will lead to a solution of the above reaction. In the meantime, since during the course of the investigation a considerable quantity of ethyl α-cyano-γ-phenylacetoacetate has been prepared, we give in the present paper an account of its properties and those of some of its derivatives, since the published data concerning them have been in some instances incorrectly recorded.

Ethyl α-cyano-γ-phenylacetoacetate was originally prepared by Haller (*Ber.*, 1888, **21**, 644) by the action of phenylacetyl chloride on the sodium compound of ethyl cyanoacetate, and was described as a yellow oil not capable of being distilled under diminished pressure without undergoing decomposition. We have prepared large quantities of this ethyl salt in a crystalline condition by employing the following modification of Haller's process. Two molecular proportions of the sodium compound were condensed with one molecular equivalent of the acid chloride, when the following reactions ensued :

(1) $CH_2Ph\cdot COCl + CHNa(CN)\cdot CO_2Et =$

$$CH_2Ph\cdot CO\cdot CH(CN)\cdot CO_2Et + NaCl.$$

(2) $CH_2Ph\cdot CO\cdot CH(CN)\cdot CO_2Et + CHNa(CN)\cdot CO_2Et =$
$CH_2Ph\cdot CO\cdot CNa(CN)\cdot CO_2Et + CH_2(CN)\cdot CO_2Et$.

The product therefore consisted of the sodium compound of ethyl α-cyano-γ-phenylacetoacetate and ethyl cyanoacetate. Since the sodium derivative is quite stable in aqueous solution, it dissolved on adding water, and on extracting with ether the whole of the ethyl cyanoacetate was removed, leaving an aqueous solution from which, on acidifying, ethyl α-cyano-γ-phenylacetoacetate was precipitated as an almost colourless oil. The ethyl salt prepared in this way was found to distil without decomposition, yielding a colourless distillate which solidified on cooling.

The salts of ethyl α-cyano-γ-phenylacetoacetate are remarkably stable substances, and the ammonium salt can be recrystallised from hot water without change. The action of alkyl iodides on the silver salt gives results of some interest, since the salt reacts as an allelotropic mixture of the two forms:

$CH_2Ph\cdot C(OAg){:}C(CN)\cdot CO_2Et$ and $CH_2Ph\cdot CO\cdot CAg(CN)\cdot CO_2Et$.

Thus, when the silver salt is treated in dry ether with ethyl iodide, an ethyl derivative can be prepared which, although distilling at a constant temperature, is nevertheless a mixture of the two compounds:

$CH_2Ph\cdot C(OEt){:}C(CN)\cdot CO_2Et$ and $CH_2Ph\cdot CO\cdot CEt(CN)\cdot CO_2Et$,

a fact which is proved in the following way. The oil showed no signs of crystallising even when kept for several weeks in the ice-chest, but ultimately, during an experiment on the action of bromine in chloroform solution on the oil, crystals were obtained which when added to the oil immediately started crystallisation. After the lapse of a month, when the growth of the crystals appeared to have ceased, they were separated from the supernatant oil by means of porous porcelain, recrystallised, and obtained in well-defined crystals melting sharply at 66°.

These crystals are the ethoxy-derivative,

$CH_2Ph\cdot C(OEt){:}C(CN)\cdot CO_2Et$,

a fact which is clearly proved by their behaviour on warming with dilute aqueous potassium hydroxide, when hydrolysis ensues in accordance with the equation:

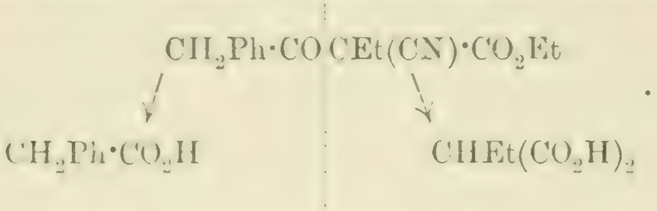
$CH_2Ph\cdot C(OEt){:}C(CN)\cdot CO_2Et + KOH =$
$CH_2Ph\cdot C(OK){:}C(CN)\cdot CO_2Et + EtOH$,

yielding a potassium compound which on acidifying is transformed into ethyl α-cyano-γ-phenylacetoacetate. On prolonged boiling with aqueous alkali, the hydrolysis of course proceeds further, and the potassium salts of phenylacetic and malonic acids are the sole products.

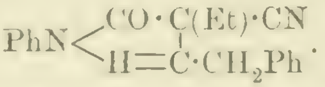
Moreover, the ethoxy-derivative does not combine with phenylhydrazine to form a pyrazolone, a reaction which is readily effected with ethyl α-cyano-γ-phenyl-α-ethylacetoacetate, but it yields a well-defined anilide melting at 85°.

The oil which had been separated from the crystals by the aid of porous porcelain was extracted and isolated. It boiled constantly at 190—191° (20 mm.), but could not be induced to crystallise; moreover, the addition of a crystal of the ethoxy-derivative failed to induce crystallisation. It is evident that this liquid is the ethyl derivative of the formula $CH_2Ph\cdot CO\cdot CEt(CN)\cdot CO_2Et$, for the following reasons:

(1) On alkaline hydrolysis, the ethyl salt is converted into phenylacetic acid and ethylmalonic acid in accordance with the scheme:



(2) On treatment with phenylhydrazine, it yields 4-cyano-1-phenyl-3-benzyl-4-ethylpyrazolone:



$$PhN{<}\begin{matrix}CO\cdot C(Et)\cdot CN\\ N{=}C\cdot CH_2Ph\end{matrix}.$$

(3) On treatment with aniline, it yields an anilide melting at 129°, quite different from that derived from the isomeric ethoxy-derivative. Under the experimental conditions described, the *O*-ethyl derivative is produced to a much greater extent than the *C*-ethyl compound, the proportion being about 4 : 1. We could not, however, be quite certain that the *C*-ethyl compound was entirely free from the *O*-derivative.

This is therefore another instance of "anomalous replacement" (compare Lander, Trans., 1903, **83**, 415), of which there are now so many, especially among the nitrogen compounds.

Many experiments were tried with the object of converting ethyl α-cyano-γ-phenylacetoacetate into the corresponding amino-derivative, but without success. The ammonium salt, which crystallised well from water, probably has the formula $CH_2Ph\cdot C(ONH_4)\colon C(CN)\cdot CO_2Et$, and it was hoped that by eliminating water from this salt an amino-derivative of the formula $CH_2Ph\cdot C(NH_2)\colon C(CN)\cdot CO_2Et$ would be obtained which would either be identical or isomeric with ethyl β-imino-α-cyano-γ-phenylbutyrate, $CH_2Ph\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et$, which had been previously prepared by the interaction of phenylacetonitrile and the sodium compound of ethyl cyanoacetate (Trans., 1906, **89**, 1916). The ammonium salt, however, evolved ammonia on being heated at 100°, being transformed into the ethyl salt from which it was derived; acetic anhydride and other dehydrating agents brought about a similar result, and when the salt was rapidly distilled it was partly transformed into phenylacetamide and partly into a substance which is probably the amide of α-cyano-γ-phenylacetoacetic acid. The cause of this decomposition is most likely due to the fact that it is impossible to eliminate from the ammonium salt the one molecule of water of crystallisation with which it is always accompanied.

Preparation of Ethyl α-Cyano-γ-phenylacetoacetate, $CH_2Ph\cdot CO\cdot CH(CN)\cdot CO_2Et$.

In order to obtain this substance, the dried sodium compound of ethyl cyanoacetate was first prepared by adding the ethyl salt to a solution containing the requisite quantity of sodium dissolved in ethyl alcohol, then adding an equal volume of dry ether, filtering, washing thoroughly with dry ether, and, finally, drying in an evacuated desiccator over sulphuric acid. Two molecular proportions of the dry salt were then taken, suspended in dry ether, and cautiously mixed in a flask fitted with a water condenser with one molecular proportion of phenylacetyl chloride. The reaction started at once, and was practically at an end shortly after the last portion of phenylacetyl chloride had been added, although, in order to make certain that the condensation had finished, an hour was allowed to elapse before the product was worked up. Water was then added, the mixture well shaken, and the ethereal layer separated. The product, which consisted of a mixture of ethyl cyanoacetate and the sodium compound of ethyl-α-cyano-γ-phenylacetoacetate formed in accordance with the equations given on pp. 1899 and 1900, had therefore been separated by the above process, the ethyl cyanoacetate remaining dissolved in the ether and the sodium compound of the condensation product remaining in solution in the aqueous extract, which was extracted once with ether and then made acid with hydrochloric acid. The heavy oil which then separated was extracted with ether, the ethereal solution, dried, and evaporated, when a residue was left which distilled constantly at 178° (20 mm.) as a colourless oil which became solid on cooling. The solid was spread on a porous plate to remove oily impurities and then crystallised from ethyl alcohol, separating from the well-cooled solution in large, colourless prisms melting at 26°:

0·1582 gave 0·3894 CO_2 and 0·0826 H_2O. C = 67·17 ; H = 5·80.
$C_{13}H_{13}O_3N$ requires C = 67·5 ; H = 5·6 per cent.

Ethyl α-cyano-γ-phenylacetoacetate in alcoholic solution gives a deep red colour with ferric chloride. It is a strong acid and readily decomposes alkaline carbonates. The sodium and potassium salts, prepared either by the action of the carbonates or by the action of the hydroxides, are precipitated from their solutions by excess of the reagent, but they are oily substances difficult to obtain pure.

The *ammonium* salt, $C_{13}H_{16}O_3N_2,H_2O$, is best prepared in quantity by suspending 20 grams of the ethyl salt in 150 c.c. of water heated to 50°, adding excess of ammonia, and allowing the clear solution to stand, when colourless crystals of the salt slowly separate. It crystallises from warm water in slender needles without undergoing appreciable dissociation, although, when boiled, the solution slowly evolves ammonia and becomes cloudy owing to the separation of ethyl α-cyano-γ-phenylacetoacetate :

0·2985 gave 27·8 c.c. of nitrogen at 21° and 767 mm. N = 10·71.

$C_{13}H_{18}O_4N_2$ requires N = 10·5 per cent.

It was not found possible to eliminate the water of crystallisation from the ammonium salt, since, when heated at 100° or when treated with dehydrating agents, it gradually lost ammonia, being reconverted into the ethyl salt from which it was derived.

The *silver* salt, $C_{13}H_{12}O_3NAg$, was obtained as a white precipitate on adding a solution of silver nitrate to an aqueous solution of the ammonium salt :

0·2586 gave 0·0824 Ag. Ag = 31·86.

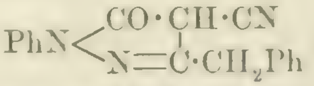
$C_{13}H_{12}O_3NAg$ requires Ag = 31·95 per cent.

α-Cyano-γ-phenylacetoacetanilide, $CH_2Ph\cdot CO\cdot CH(CN)\cdot CO\cdot NHPh$, can be prepared by boiling ethyl α-cyano-γ-phenylacetoacetate with excess of aniline for a few minutes and pouring the product into excess of dilute hydrochloric acid. The oil which remains undissolved rapidly crystallises, and can be purified by recrystallisation from alcohol, from which solvent it separates in long, colourless needles melting at 145° :

0·1770 gave 0·4769 CO_2 and 0·0843 H_2O. C = 73·48 ; H = 5·23.

$C_{17}H_{14}O_2N_2$ requires C = 73·4 ; H = 5·0 per cent.

The anilide gives a deep red colour in alcoholic solution with ferric chloride, and is soluble in aqueous solutions of caustic alkalis. On hydrolysis with dilute sulphuric acid, it is completely decomposed into aniline, malonic acid, and phenylacetic acid.

4-Cyano-1-phenyl-3-benzylpyrazolone,  $PhN{<}\begin{matrix}CO\cdot CH\cdot CN\\ |\\ N{=}C\cdot CH_2Ph\end{matrix}$, is prepared by the action of phenylhydrazine on ethyl α-cyano-γ-phenylacetoacetate. The ethyl salt is dissolved in glacial acetic acid and, after being mixed with a solution of phenylhydrazine in acetic acid, is boiled for a few minutes. On cooling, a copious, crystalline precipitate separates, which can be crystallised from absolute alcohol, when it is obtained in slender, colourless plates melting at 173° :

0·2233 gave 30·8 c.c. of nitrogen at 20° and 754 mm. N = 15·17.
$C_{17}H_{13}ON_3$ requires N = 15·2 per cent.

Action of Heat on the Ammonium Salt of Ethyl α-Cyano-γ-phenylacetoacetate.

As already mentioned, the above ammonium salt crystallises with one molecule of water of crystallisation, from which it cannot be freed without at the same time undergoing decomposition. Numerous experiments were tried with the object of causing the compound to lose water and pass into the corresponding amino-derivative, amongst which was the action of heat under different conditions. When the ammonium salt is heated at 100° under ordinary pressure, ammonia is eliminated and ethyl α-cyano-γ-phenylacetoacetate is formed. When, however, it is rapidly heated under 20 mm. pressure, a curious decomposition takes place leading to the formation of phenylacetamide and another substance which seems to be the amide of α-cyano-γ-phenylacetoacetic acid. The ammonium salt which had been placed for several days in an evacuated desiccator over sulphuric acid was heated at 150° under a pressure of 29 mm. in an inverted distillation flask until the evolution of gas had ceased, when the residue, which solidified on cooling, was freed from oil by spreading on a porous plate. The white, crystalline solid was then treated with dilute sodium carbonate solution and filtered, the insoluble matter being recrystallised from water, from which it separated in lustrous plates melting at 155°:

0·1747 gave 0·4543 CO_2 and 0·1079 H_2O. C = 70·92; H = 6·75.
C_8H_9ON requires C = 71·1; H = 6·7 per cent.

The compound gave phenylacetic acid on hydrolysis with aqueous potassium hydroxide, and was therefore phenylacetamide.

The sodium carbonate solution from the above substance yielded a crystalline precipitate on acidifying, which was collected and recrystallised from alcohol, when it was obtained in lustrous laminæ melting at 167°:

0·1724 gave 0·4121 CO_2 and 0·0801 H_2O. C = 65·19; H = 5·16.
0·1558 ,, 18·3 c.c. of nitrogen at 15° and 770 mm. N = 13·94.
$C_{11}H_{10}O_2N_2$ requires C = 65·3; H = 4·9; N = 13·8 per cent.

The compound gives a deep red coloration with ferric chloride, and is slowly hydrolysed on prolonged boiling with aqueous potassium hydroxide, yielding phenylacetic acid and malonic acid, but the hydrolysis takes place with great difficulty, much more so than would have been expected in the case of an amide, and it is therefore possible that this compound may have a constitution other than that assigned to it by us.

The action of dehydrating agents was also tried in order to eliminate water from the ammonium salt, but without avail. Thus, for example, boiling with acetic anhydride completely transformed the salt into ammonium acetate and ethyl α-cyano-γ-phenylacetoacetate, the action of other dehydrating agents producing a similar result.

Preparation of Ethyl α-Cyano-γ-phenyl-α-ethylacetoacetate, $CH_2Ph·CO·CEt(CN)·CO_2Et$ *and Ethyl α-Cyano-β-ethoxy-γ-phenylcrotonate,* $CH_2Ph·C(OEt)\colon C(CN)·CO_2Et$.

The sodium compound of ethyl α-cyano-γ-phenylacetoacetate does not react with alkyl iodides, and in order to prepare the ethyl derivative it is necessary to prepare the silver compound of the ethyl salt and then to treat it, suspended in ether, with the alkyl iodide. The well-dried silver compound, prepared in the manner already described on p. 1903, was suspended in dry ether in a flask fitted with a reflux condenser and, after being mixed with excess of ethyl iodide, heated on the water-bath until a test portion indicated that all the silver compound had been converted into silver iodide. The product was then filtered and the filtrate evaporated free from ether, when an oily residue remained which distilled constantly at 191° (20 mm.). The following analysis proved that this compound possessed the formula $C_{15}H_{17}O_3N$:

0·1978 gave 0·5015 CO_2 and 0·1205 H_2O. C = 69·21 ; H = 6·77.

$C_{15}H_{17}O_3N$ requires C = 69·5 ; H = 6·5 per cent.

Ethyl α-Cyano-β-ethoxy-γ-phenylcrotonate.—The oil described above showed no signs of crystallising even when cooled to a low temperature, and it was therefore concluded that the compound was a liquid. Later, however, an experiment was tried with the object of ascertaining the action of bromine in chloroform solution on the ethyl salt. It was found that only a trace of the halogen was absorbed, but on evaporating the product free from chloroform a residue was obtained which rapidly solidified, and a crystal added to the liquid ethyl compound caused it to crystallise slowly. It was left for a month in the ice-chest, when, since the growth of the crystals appeared to have ceased, it was spread on porous porcelain to remove the considerable quantity of oil which had not solidified and then recrystallised from light petroleum (b. p. 80—90°) containing a little benzene, being obtained in large, colourless prisms melting at 66°:

0·1583 gave 0·4042 CO_2 and 0·0953 H_2O. C = 69·63 ; H = 6·68.

$C_{15}H_{17}O_3N$ requires C = 69·5 ; H = 6·5 per cent.

The ethyl salt is quite insoluble in alkaline carbonates and in cold caustic alkalis. It gives no coloration in alcoholic solution with ferric chloride.

α-Cyano-β-ethoxy-γ-phenylcrotonanilide,

$CH_2Ph\cdot C(OEt):C(CN)\cdot CO\cdot NHPh$,

was prepared by boiling the above ethyl salt with excess of aniline for a few minutes and pouring the product into dilute hydrochloric acid. The oil which remained undissolved quickly solidified, and was purified by recrystallisation from alcohol, from which solvent it separated in colourless, rhombic prisms melting at 85°:

0·2148 gave 17·0 c.c. of nitrogen at 19° and 768 mm. N = 9·19.

$C_{19}H_{18}O_2N_2$ requires N = 9·1 per cent.

When ethyl α-cyano-β-ethoxy-γ-phenylcrotonate is warmed with dilute aqueous potassium hydroxide, it rapidly passes into solution, and, on acidifying the product immediately after complete solution has been effected, an oil is precipitated which on extraction with ether furnishes ethyl α-cyano-γ-phenylacetoacetate melting at 26°:

0·1685 gave 0·4177 CO_2 and 0·0873 H_2O. C = 67·60; H = 5·75.

$C_{13}H_{13}O_3N$ requires C = 67·5; H = 5·6 per cent.

The compound was further identified by its conversion into the anilide melting at 145°.

If the heating is continued after all the ethyl salt has dissolved in the aqueous potassium hydroxide, ammonia is evolved, and the final product consists of phenylacetic acid and malonic acid.

Ethyl α-Cyano-α-ethyl-γ-phenylacetoacetate.—The porous porcelain, which had been used to dry the crystals described above, was broken into small pieces and extracted in a Soxhlet apparatus by means of ether. The ethereal solution on evaporation yielded an oil which distilled at 190—191° (20 mm.) as a viscid, colourless liquid:

0·1977 gave 0·5041 CO_2 and 0·1187 H_2O. C = 69·54; H = 6·67.

$C_{15}H_{17}O_3N$ requires C = 69·5; H = 6·5 per cent.

The compound, which was quite insoluble in dilute aqueous potassium hydroxide even on warming, could not be induced to solidify even in a freezing mixture. It gave no coloration with ferric chloride.

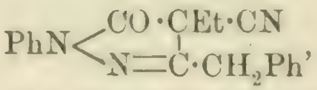
α-Cyano-α-ethyl-γ-phenylacetoacetanilide,

$CH_2Ph\cdot CO\cdot CEt(CN)\cdot CO\cdot NHPh$,

was prepared by boiling a solution of the ethyl salt in aniline for a few minutes, and pouring the product into excess of dilute hydrochloric acid. The crystalline substance which remained undissolved was filtered and purified by recrystallisation from alcohol, when it was obtained in colourless needles melting at 129°:

0·2078 gave 16·6 c.c. of nitrogen at 20° and 769 mm. N = 9·23.

$C_{19}H_{18}O_2N_2$ requires N = 9·1 per cent.

4-*Cyano-1-phenyl-3-benzylethylpyrazolone*,  $PhN\!<\!\begin{matrix}CO\cdot \overset{}{C}Et\cdot CN\\ N{=}\overset{|}{C}\cdot CH_2Ph\end{matrix}$, was prepared by heating a solution of the ethyl salt in acetic acid with a solution of phenylhydrazine acetate. On cooling, crystals slowly separated, which when purified by recrystallisation from alcohol yielded colourless needles melting at 167°:

0·2219 gave 27·1 c.c. of nitrogen at 19° and 757 mm. $N = 14{\cdot}00$.
$C_{19}H_{17}ON_3$ requires $N = 13{\cdot}9$ per cent.

Hydrolysis of Ethyl a-Cyano-a-ethyl-γ-phenylacetoacetate to Phenylacetic and Ethylmalonic Acids.

This hydrolysis was effected by dissolving the ethyl salt in a methyl-alcoholic solution of one and a-half times the calculated quantity of potash, and heating on the water-bath until the evolution of ammonia had ceased. The product was then poured into an evaporating basin, freed from methyl alcohol on the water-bath, and, after dilution, acidified with hydrochloric acid. The white precipitate was filtered and crystallised from dilute alcohol, when the characteristic plates of phenylacetic acid were obtained.

The aqueous residue was extracted with ether and the ethereal solution dried and evaporated, when the solid residue on crystallisation from concentrated hydrochloric acid yielded small plates melting at 112°:

0·1801 gave 0·2983 CO_2 and 0·0979 H_2O. $C = 45{\cdot}17$; $H = 6{\cdot}04$.
$C_5H_8O_4$ requires $C = 45{\cdot}4$; $H = 6{\cdot}1$ per cent.

The compound was therefore ethylmalonic acid.

MANCHESTER UNIVERSITY.

CLXXXV.—*Chemical Examination of the Root and Leaves of Morinda longiflora.*

By MARMADUKE BARROWCLIFF and FRANK TUTIN.

SEVERAL plants belonging to the genus *Morinda* (Nat. Ord. *Rubiaceæ*) have from time to time attracted the attention of chemists, chiefly on account of the tinctorial properties possessed by them. The Indian dye-stuff "Suranji," which consists of the roots of *M. citrifolia* and *M. tinctoria*, was investigated by Anderson (*Annalen*, 1849, **71**, 216), who obtained from it a substance designated "morindin," which, when heated, gave a sublimate of a red compound named "morindon." Subsequent workers have shown that morindin is a glucoside, $C_{26}H_{28}O_{14}$, and that morindone, yielded by its hydrolysis, is a trihydroxymethylanthraquinone. An exhaustive examination of "Mang-Koudu," the root-bark of *M. umbellata*, was conducted by Perkin and Hummel (Trans., 1894, **65**, 857), who obtained from it morindin, morindone, and five other anthraquinone derivatives. More recently, Oesterle (*Arch. Pharm.*, 1907, **245**, 287) has examined the wood of *M. citrifolia*, and obtained from it a dihydroxymethoxyanthraquinone.

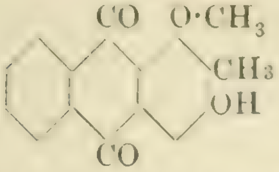
The West African plant, *Morinda longiflora*, G. Don, was brought to our notice by an article in the *Journal of the Society of Arts* (1905, **53**, 1069), where it is referred to, under the name of "Ojuologbo"—Woody Vine, as one of the most valuable plants of that region, and is stated to be used as a medicine by nearly all West African tribes.

Through the kindness of Dr. W. Renner, Medical Officer, Colonial Hospital, Freetown, Sierra Leone, we were supplied with a quantity of the roots and leaves of "Ojuologbo," and the identity of the material thus obtained with the products of *Morinda longiflora* was kindly confirmed by Mr. E. M. Holmes, F.L.S. A complete botanical description of this plant may be found in the *Flora of Tropical Africa*, by Daniel Oliver, F.R.S., Vol. III, p. 192, London, 1877, where it is stated to be known under the native name of "Mbogga."

As a preliminary test, the leaves and root were each examined for the presence of an alkaloid, but with a negative result. The ground materials were subsequently extracted with alcohol, and the resulting extracts separately investigated.

On examining the extract yielded by the root, no morindin or morindone was obtained, but a quantity of a *hydroxymethoxymethylanthraquinone* and a small amount of a monomethyl ether of alizarin were isolated. The root also yielded, in addition to resins and other amorphous products, small quantities of formic, acetic, butyric, palmitic, and citric acids, a little of a phytosterol, $C_{27}H_{46}O$ (m. p. 130°), and a considerable amount of a sugar which yielded *d*-phenylglucosazone (m. p. 216°.)

The hydroxymethoxymethylanthraquinone, $C_{16}H_{12}O_4$, forms yellow needles which melt at 290°, and gives an *acetyl* derivative melting at 173°. When heated with 70 per cent. sulphuric acid, it yields a dihydroxy-compound identical with the 1 : 3-dihydroxy-2-methylanthraquinone prepared by Schunck and Marchlewski (Trans., 1894, **65**, 182). It must, therefore, be represented by one of the following formulæ:



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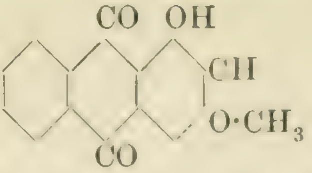

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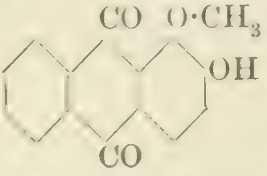
On heating with hydriodic acid it yields a *dihydroxymethylanthranol*, $C_{15}H_{12}O_3$ (m. p. 235°), and on methylation gives 1 : 3-*dimethoxy-2-methylanthraquinone* (m. p. 181°)—a compound which is also readily obtained from the 1 : 3-dihydroxy-2-methylanthraquinone prepared by Schunck and Marchlewski.

The monomethyl ether of alizarin present in "Ojuologbo" root was obtained in needles (m. p. 175°), and yielded an acetyl derivative melting at 209°. It was shown to be identical with the compound of this nature isolated by Perkin and Hummel (Trans., 1893, **63**, 1174) from the root of *Oldenlandia umbellata* ("Chay root").

Alizarin was methylated by Schunck (*Mem. Manchester Phil. Soc.*, 1873), also by Schunck and Marchlewski (*loc. cit.*), and more recently by Gräbe and Aders (*Annalen*, 1901, **318**, 369), but the product was, in all cases, a monomethyl ether melting at 228—229°. Since, as was shown by Kostanecki and Dreher (*Ber.*, 1893, **26**, 76), the hydroxyl group in the monohydroxyxanthones will not undergo methylation when it is situated in the 1-position with respect to the carbonyl group, whereas it readily does so when in the 2-, 3-, or 4-position, it was suggested by Schunck and Marchlewski that the hydroxyanthraquinones might show a similar behaviour. They therefore concluded that the monomethylalizarin prepared by them was probably the 2-methoxy-compound. This opinion, which was also shared by Gräbe and Aders (*loc. cit.*), would lead to the conclusion that the monomethylalizarin occurring in *Morinda longiflora* and *Oldenlandia umbellata* possesses the following formula :



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It would appear, however, that the hydroxyanthraquinones, on methylation, may not always exhibit a behaviour analogous to that of the hydroxyxanthones, as it has been shown in this investigation that 1 : 3-dihydroxy-2-methylanthraquinone readily undergoes complete methylation. It is impossible, therefore, from the above considerations to arrive at a safe conclusion regarding the position occupied by the methoxyl group in the above-described methyl ether of alizarin.

The extract obtained from the "Ojuologbo" leaves differed from that yielded by the root, inasmuch as it contained a considerable proportion of material which was soluble in petroleum. This petroleum extract yielded palmitic acid, together with traces of acetic and formic acids, and a small amount of the hydrocarbon hentriacontane. The leaves were also found to contain some of the previously-mentioned hydroxymethoxymethylanthraquinone (m. p. 290°), but their most interesting constituent is a new, crystalline *alcohol*, which it is proposed to designate *morindanol.* This substance possesses the formula $C_{38}H_{62}O_4$, melts at 278°, and has $[\alpha]_D + 65 \cdot 9°$. It yields *methylmorindanol*, $C_{38}H_{61}O_3 \cdot O \cdot CH_3$ (m. p. 116°), on treatment with sodium ethoxide and methyl iodide.

Morindanol is represented by the same general formula, $C_nH_{2n-14}O_4$, as three other crystalline alcohols which have recently been isolated in these laboratories, namely, lippianol, $C_{25}H_{36}O_4$ (m. p. 300—308°; $[\alpha]_D + 64 \cdot 9°$), obtained from *Lippia scaberrima*, Sonder (Power and Tutin, *Arch. Pharm.*, 1907, **245**, 344), and micromerol, $C_{33}H_{52}O_4$ (m. p. 277°; $[\alpha]_D + 57°$), and micromeritol, $C_{30}H_{46}O_4$ (m. p. 294—296°; $[\alpha]_D + 61 \cdot 4°$), both recently isolated by Drs. F. B. Power and A. H. Salway from *Micromeria Chamissonis.* These four substances, moreover, exhibit a marked similarity in properties, and it would therefore appear probable that they are chemically related. No similar compounds appear previously to have been described.

In order to ascertain whether "Ojuologbo" possesses any pronounced physiological action, the following experiments were conducted for us by Mr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, to whom our thanks are due. Amounts of the extracts corresponding respectively to 17 grams of the dried leaves and to 7·5 grams of the dried root were administered to small dogs, but no definite effects of any kind could be observed.

EXPERIMENTAL.

I. *Examination of the Root.*

For the purpose of this investigation, a quantity (10·9 kilograms) of the finely-ground root was completely extracted by continuous percolation with hot alcohol. The liquid thus obtained was freed from the greater part of the solvent, the resulting dark brown extract then mixed with water, and distilled with steam until the liquid flowing from the condenser was no longer acid. The distillate contained drops of a heavy, yellow oil possessing a peculiar odour. It was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. The deep red, alkaline liquid thus obtained yielded, on acidification and extraction with ether, a small quantity of a red oil which deposited crystals on standing. These, after being separated and recrystallised from alcohol, melted at 59—60°, and apparently consisted of palmitic acid.

The ethereal liquid which had been freed from acids by means of sodium carbonate yielded a very small amount of a yellow essential oil, whilst the aqueous portion of the distillate was found to contain formic, acetic, and butyric acids.

The contents of the distillation flask consisted of a quantity of resinous matter, and a dark-coloured, aqueous liquid. The latter was decanted from the resin, which was then washed several times with hot water.

Examination of the Resins.

The resin was boiled with several successive portions of alcohol, and the liquids filtered. In this way there were obtained a dark coloured solution, which deposited a small amount of a solid on standing, and a quantity of an amorphous, brown powder. The latter product was very sparingly soluble in alcohol or glacial acetic acid, and insoluble in the other usual solvents. Nothing crystalline could be separated from it, and, in view of the possibility of its being a glucoside, it was submitted to the action of dilute alcoholic hydrochloric acid, but with a negative result.

The solution of that portion of the resins which had been dissolved by treatment with alcohol was evaporated on purified sawdust, and extracted successively in a Soxhlet apparatus with light petroleum (b. p. 33—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resins.

This was small in amount. The greater portion of it was soluble in a solution of sodium carbonate, and a further quantity was dissolved by cold aqueous potassium hydroxide. Nothing crystalline was obtained from it.

Ethereal Extract of the Resins.

This weighed 35 grams. On attempting to redissolve it in ether, a portion did not readily pass into solution, and this was collected on a filter and independently examined. The ethereal filtrate, containing the more readily soluble constituents of the extract, was shaken with several successive portions of a solution of sodium carbonate, and the alkaline liquids thus obtained, which were all dark red, were examined separately.

Isolation of a Hydroxymethoxymethylanthraquinone, $C_{16}H_{12}O_4$.

On acidifying the first two sodium carbonate extracts, a viscid, oily substance separated, but the liquids from the subsequent shakings with this alkali yielded a precipitate of a dark yellow solid. This was dissolved in hot alcohol, from which, on cooling, it separated in brown crystals melting at about 280° As these crystals could not readily be purified, the entire amount of the substance was dissolved in acetic anhydride and the mixture boiled. The resulting *acetyl* derivative was crystallised from ethyl acetate, when it was obtained in deep yellow needles melting at 173°:

0·1109 gave 0·2824 CO_2 and 0·0448 H_2O. C = 69·4; H = 4·5.
0·1052 ,, 0·2673 CO_2 ,, 0·0427 H_2O. C = 69·3; H = 4·5.
$C_{18}H_{14}O_5$ requires C = 69·7; H = 4·5 per cent.

The portion of the ethereal extract of the resins which was only sparingly soluble in ether, and which was separated as described above, was found to consist of the substance which yielded this acetyl derivative, as on heating it with acetic anhydride the same product (m. p. 173°) was obtained.

The pure acetyl derivative was hydrolysed, and the product crystallised from absolute alcohol. It separated in golden-yellow needles melting at 290°:

0·1066 gave 0·2780 CO_2 and 0·0444 H_2O. C = 71·1; H = 4·6.
0·1142 ,, 0·2994 CO_2 ,, 0·0463 H_2O. C = 71·5; H = 4·5.
$C_{16}H_{12}O_4$ requires C = 71·6; H = 4·5 per cent.

No substance of the formula $C_{16}H_{12}O_4$ and possessing properties agreeing with those of this compound has hitherto been described. A methoxyl determination by means of Perkin's modification of Zeisel's method gave the following result:

0·2585 gave 0·2275 AgI. $CH_3 \cdot O = 11·6$.
$C_{15}H_9O_3 \cdot O \cdot CH_3$ requires $CH_3 \cdot O = 11·6$ per cent.

The flask which had been employed in this estimation contained, together with the hydriodic acid, a quantity of a solid *substance*. This was collected, and crystallised from ethyl acetate, when it was obtained in dark yellow needles melting at 235°:

0·1030 gave 0·2802 CO_2 and 0·0446 H_2O. C = 74·2; H = 4·8.
$C_{15}H_{12}O_3$ requires C = 75·0; H = 5·0 per cent.

A further quantity of this substance (m. p. 235°) was prepared, and oxidised with chromic acid, when a compound was obtained which crystallised from ethyl acetate in deep golden leaflets melting at 290°. The latter substance was also produced, and in much better yield, on heating the original methoxy-derivative with 70 per cent. sulphuric acid. It was analysed with the following result:

0·0885 gave 0·2290 CO_2 and 0·0326 H_2O. C = 70·6 ; H = 4·1.

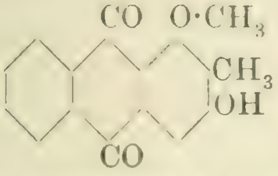
$C_{15}H_{10}O_4$ requires C = 70·9 ; H = 3·9 per cent.

This compound agrees in composition and properties with the 1 : 3-dihydroxy-2-methylanthraquinone prepared by Schunck and Marchlewski (Trans., 1894, **65**, 182), and is evidently identical with it. In order to confirm this conclusion the acetyl derivative was prepared, and was obtained in slender, pale yellow needles melting at 225°,—the temperature recorded by Schunck and Marchlewski for the melting point of the acetyl derivative of the substance prepared by them:

0·1208 gave 0·2992 CO_2 and 0·0462 H_2O. C = 67·5 ; H = 4·2.

$C_{15}H_8O_4(CO\cdot CH_3)_2$ requires C = 67·5 ; H = 4·1 per cent.

The yellow substance melting at 290°, isolated from the root of *Morinda longiflora*, must, therefore, be a *hydroxymethoxymethylanthraquinone* possessing a constitution represented by one of the following formulæ:



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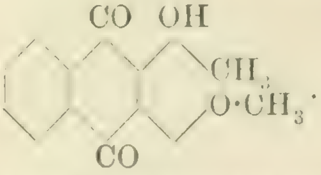

The compound, $C_{17}H_{12}O_3$ (m. p. 235°), which was formed from this hydroxymethoxymethylanthraquinone by the action of hydriodic acid, and which yielded 1 : 3-dihydroxy-2-methylanthraquinone on oxidation, must, therefore, be a *dihydroxymethylanthranol*.

1 : 3-*Dimethoxy-2-methylanthraquinone*.—On solution in alcohol and treatment with sodium ethoxide and methyl iodide, the hydroxymethoxymethylanthraquinone yielded 1 : 3-*dimethoxy-2-methylanthraquinone*. This new compound is also readily produced in a similar manner from 1 : 3-dihydroxy-2-methylanthraquinone. It crystallises in golden-coloured needles melting at 181°:

0·1142 gave 0·3020 CO_2 and 0·0537 H_2O. C = 72·1 ; H = 5·2.

$C_{17}H_{14}O_4$ requires C = 72·3 ; H = 5·0 per cent.

Isolation of a Monomethyl Ether of Alizarin.

The oily product which separated on acidifying the first two alkaline liquids obtained by shaking the ethereal solution of the readily soluble portion of the ether extract of the resins with sodium carbonate, as already described, deposited no solid on standing. It was, however, thought probable that it might contain some of the above-described hydroxymethoxymethylanthraquinone, or other phenolic substance, together with carboxylic acids. It was therefore heated with acetic anhydride, the product dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate. Acidification of the dark-coloured alkaline liquid thus obtained yielded a viscid substance from which nothing crystalline could be separated, but on evaporating the ethereal solution containing the non-acidic, acetylated product an oily liquid was obtained which deposited a small quantity of a solid on standing. This was collected, and, after several crystallisations from ethyl acetate, was obtained in pale yellow needles melting sharply at 209°. It was hydrolysed with alcoholic potash, and the product crystallised from ethyl acetate, when it formed yellow needles melting at 175°. Unlike its acetyl derivative, this substance is freely soluble in alcohol.

On dissolving a trace of this compound in concentrated sulphuric acid a brownish-red colour was produced, which, on heating the liquid to 150°, changed to an intense red. It dissolved in a solution of barium hydroxide with a red colour, and on boiling the liquid for some time a violet-coloured precipitate was deposited. The substance melting at 175° was analysed with the following result:

0·0629 gave 0·1638 CO_2 and 0·0228 H_2O. $C = 71·0$; $H = 4·0$.

$C_{15}H_{10}O_4$ requires $C = 70·9$; $H = 3·9$ per cent.

The composition and properties of this substance agree with those of the monomethyl ether of alizarin which was isolated by Perkin and Hummel (Trans., 1893, 63, 1174) from the root of *Oldenlandia umbellata*, Linn. ("Chay root"),—a plant belonging to the same natural order (*Rubiaceæ*) as *Morinda longiflora*. Unfortunately, sufficient material was not available to permit of our making a methoxyl determination. The melting point found by Perkin and Hummel for the compound isolated by them is 3° higher than that found for our substance, but the acetyl derivative of each preparation melts at 209°. No doubt can therefore be entertained regarding the identity of the above-described substance, $C_{15}H_{10}O_4$, with the monomethyl ether of alizarin obtained from "Chay root."

The oily liquid, from which the acetyl derivative of the monomethyl ether of alizarin had been separated, was hydrolysed. The product yielded a further quantity of the hydroxymethoxymethylanthraquinone, but no other solid substance could be obtained from it.

After the ethereal solution of the readily soluble portion of the ether extract of the resins had been treated with a solution of sodium carbonate, as already described, it was shaken with a dilute solution of sodium hydroxide. The product which separated on acidifying the alkaline liquid thus obtained was only small in amount, and nothing crystalline could be obtained from it. The ethereal liquid, which was now free from substances of an acidic or phenolic nature, was evaporated, when a product was obtained which deposited a solid on standing. This was several times crystallised from alcohol, and obtained in colourless leaflets melting at 130°. On treatment with acetic anhydride and sulphuric acid, it gave the colour reaction characteristic of the phytosterols. After drying at 110° it was analysed:

0·0828 gave 0·2533 CO_2 and 0·0889 H_2O. C = 83·4; H = 11·9.

$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resins.

The chloroform extract of the resins was small in amount, and yielded only a little of the above-described hydroxymethoxymethylanthraquinone.

The portion of the resins which was extracted by ethyl acetate amounted to 22 grams. Various attempts were made to obtain a crystalline substance from it, but without success.

The remainder of the resins, which was soluble only in alcohol, was the largest extract obtained, and amounted to 90 grams. Although submitted to a prolonged investigation, it yielded nothing crystalline.

Examination of the Aqueous Liquid.

The combined aqueous liquid and washings, which had been separated from the resins, as previously described, were filtered, and extracted five times with ether. The ethereal liquid was then shaken with six successive small portions of a solution of sodium carbonate. On acidifying the first alkaline liquid thus obtained, a dark red, oily product was precipitated, which did not solidify, but the subsequent extracts gave a yellow solid, which was found to consist of the hydroxymethoxymethylanthraquinone previously isolated from the resins.

The aqueous liquid which had been extracted with ether was treated with a solution of barium acetate until no further precipitate was formed, then filtered, and the precipitate washed. This precipitate was examined, but nothing crystalline was obtained from it. A slight excess of a solution of basic lead acetate was added to the filtrate from the barium precipitate, the resulting insoluble lead compounds collected, washed, suspended in water, decomposed by means of hydrogen sulphide, and the liquid filtered. The filtrate was concentrated, mixed with purified sawdust, and dried, after which it was extracted with various solvents. From the portion removed by means of ether, a solid was obtained which, after crystallisation from ethyl acetate, melted at 151—152° and gave the reactions of anhydrous citric acid.

The filtrate from the lead acetate precipitate was freed from lead, and concentrated. It was found to contain a large amount of a hexose, as it readily yielded *d*-phenylglucosazone melting at 216°.

II. *Examination of the Leaves.*

The ground leaves (5·8 kilograms) were completely extracted by continuous percolation with hot alcohol, the liquid concentrated, and the residual dark green extract mixed with water and distilled with steam. The distillate, on extraction with ether, gave a small amount of an essential oil possessing an unpleasant odour, and the aqueous liquid from which this had been removed was found to contain formic, acetic, and butyric acids.

The distillation flask then contained a quantity (135 grams) of dark green resin, which was separated from the aqueous liquid and well washed with hot water.

Examination of the Resins.

The resinous mass was dissolved in alcohol, the solution mixed with purified sawdust, and the mixture dried, after which it was extracted successively in a Soxhlet apparatus with light petroleum (b. p. 33—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resins.

The petroleum extract amounted to 59 grams. It was dissolved in ether and the resulting liquid extracted successively with solutions of sodium carbonate and potassium hydroxide. The products obtained by this treatment were small, and yielded nothing definite, although the liquid obtained on shaking with the latter alkali had a violet colour.

The ethereal solution was then evaporated, the residue dissolved in an alcoholic solution of potassium hydroxide, and the mixture heated for two hours. The greater part of the alcohol was then removed, water added, and the alkaline liquid extracted with ether. The ethereal liquid thus obtained yielded, on evaporation, an oily product, which was distilled under diminished pressure. The distillate deposited a solid on standing which, when crystallised from ethyl acetate, formed leaflets melting at 68°:

0·0816 gave 0·2551 CO_2 and 0·1085 H_2O. C = 85·3; H = 14·8.

$C_{31}H_{64}$ requires C = 85·3; H = 14·7 per cent.

This substance was therefore the hydrocarbon hentriacontane.

The oily liquid from which this hydrocarbon had been separated was found to contain oxygenated substances, probably alcohols, but it gave no reaction for phytosterol.

The alkaline liquid from which the hydrocarbon had been removed by means of ether was acidified, and distilled with steam. This removed a little acetic and formic acids. The contents of the distillation flask were then shaken with ether, the ethereal liquid separated, concentrated to a small bulk, and a considerable volume of light petroleum added. This caused the precipitation of a quantity of green resin, from which the petroleum liquid was decanted. The latter was then evaporated and the residue distilled under diminished pressure. The distillate, which solidified on cooling, was crystallised from methyl alcohol, when it yielded a product melting at 60°:

0·1053 gave 0·2906 CO_2 and 0·1152 H_2O. C = 75·3; H = 12·2.

$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5 per cent.

This, therefore, consisted largely of palmitic acid.

Ethereal Extract of the Resins.

This was a soft, green mass weighing 57 grams. On treating with a limited amount of ether, a quantity of a green solid remained undissolved, and was collected on a filter. The ethereal filtrate was then shaken with a solution of sodium carbonate. The alkaline liquid thus obtained yielded, on acidification, a product which appeared to consist, to a considerable extent, of the hydroxymethoxymethylanthraquinone previously isolated from the root, but it could not be purified. After extracting the ethereal liquid with sodium carbonate solution, it was washed with water, when a large quantity of chlorophyll was removed, and subsequent extraction with potassium hydroxide yielded a further quantity of a similar, uncrystallisable product. The ethereal liquid finally left on evaporation only a soft, green resin.

Isolation of a New, Crystalline Alcohol, Morindanol, $C_{38}H_{61}O_3 \cdot OH, H_2O$.

The above-mentioned sparingly soluble solid was dissolved in a considerable quantity of hot alcohol and the solution digested with animal charcoal, by which means the greater part of the green colour was removed. On concentrating the solution, an amorphous, slightly green product was obtained, which melted from 240° to 270°. This was again dissolved and treated with animal charcoal, which removed the last traces of colour, when, after repeated fractionations from alcohol, the greater part of it was obtained in colourless, glistening needles melting at 278°. The substance, after drying at 100°, was analysed:

0·1077 gave 0·3088 CO_2 and 0·1041 H_2O. C = 78·2; H = 10·7.

$C_{38}H_{62}O_4$ requires C = 78·3; H = 10·7 per cent.

The air-dried substance gave the following result:

0·1025 gave 0·2852 CO_2 and 0·0978 H_2O. C = 75·9; H = 10·6.

$C_{38}H_{62}O_4,H_2O$ requires C = 76·0; H = 10·7 per cent.

0·4808, dissolved in 100 c.c. of absolute alcohol, gave α_D + 0°38′ in a 2-dcm. tube, whence $[\alpha]_D$ + 65·9°.

The composition and properties of this substance do not agree with those of any compound previously described, and, being of an alcoholic nature, it is proposed to designate it *morindanol.*

If a small quantity of morindanol is dissolved in alcohol and ammonia added, no precipitate is produced on diluting the solution with water, even if the greater part of the alcohol has previously been evaporated. The clear liquid thus obtained seems to have the character of a colloidal solution, as no morindanol will separate from it until an aqueous solution of an electrolyte is added, and, on allowing it to stand, it forms a perfectly transparent jelly.

Methylmorindanol, $C_{38}H_{61}O_3\cdot O\cdot CH_3$.—A quantity of morindanol was dissolved in alcohol, sodium ethoxide and methyl iodide added, and the mixture heated for three hours. The product was then dissolved in ether and freed from unchanged material by means of potassium hydroxide. The *methylmorindanol* was crystallised from alcohol, when it formed rosettes of needles which melted at 116°. This substance contained no solvent of crystallisation. A methoxyl determination gave the following result:

0·1034 gave 0·0405 AgI. $CH_3\cdot O$ = 5·2.

$C_{38}H_{61}O_3\cdot O\cdot CH_3$ requires $CH_3\cdot O$ = 5·2 per cent.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resins.—These were all small in amount, and nothing crystalline could be obtained from any of them.

Examination of the Aqueous Liquid.

The aqueous liquid obtained from the extract of the leaves, as previously described, was examined in a manner similar to that recorded in connexion with the corresponding product from the root, with the exception that the treatment with barium acetate was omitted. A further quantity of the hydroxymethoxymethylanthraquinone (m. p. 290°) was obtained, and the aqueous liquid, after purification by means of basic lead acetate, yielded *d*-phenylglucosazone melting at 215°. No citric acid could be obtained from the leaves.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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CLXXXVI.—*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide. Part II. The Constitution of the Products.*

By ARTHUR LAPWORTH and ELKAN WECHSLER.

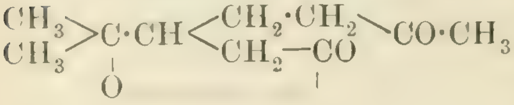
IN the previous paper (Trans., 1907, **91**, 978), it was shown that amyl nitrite in presence of sodium ethoxide converts cyanodihydrocarvone into a substance (*L*), $C_{11}H_{14}O_2N_2$, which proved to be the lactam of an amino-acid (*A*), $C_{10}H_{13}ON(NH_2)\cdot CO_2H$. By the action of dilute mineral acids on either of these, there were obtained an isomeric lactam (*L'*) and two isomeric lactonic bases (*B* and *B'*), to which the common formula $\underbrace{C_{10}H_{14}ON(NH_2)\cdot CO}_{O}$ was assigned (*loc. cit.*, p. 978 *et seq.*). The prolonged action of acids on the base (*B*) led to the formation of a substance which, although capable of forming salts with bases and expelling carbon dioxide from carbonates, was not carboxylic in character; this was referred to as "the lactonic acid," and was given the formula $\underbrace{C_{10}H_{16}O_2N(OH)\cdot CO}_{O}$. From this substance, 2:3:6-trimethylbenzoic acid was obtained by long-continued heating with concentrated hydrochloric acid.

The present paper contains an account of the experiments on the lactonic acid which led us to believe that it did not owe its acid properties to the presence of a carboxyl group, and also the results which we venture to believe establish the ultimate constitution of the principal compounds mentioned above.

In discussing the latter question, we may recall the fact that there was strong evidence in favour of the view that the NH_2 group is present in the amino-acid and in the base *B*. This we have since been able fully to confirm by preparing the *benzylidene* derivative, $\underbrace{C_{10}H_{14}ON(N{:}CHPh)\cdot CO}_{O}$, of the base by warming the latter with benzaldehyde in absence of any solvent.

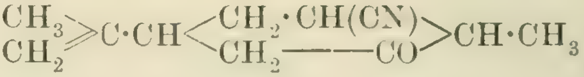
The clue to the ultimate constitution of the above compounds was obtained on an examination of the products formed when they are acted on by ferrous hydroxide in presence of alkalis. This treatment, even in the cold, leads to their decomposition, ammonia being evolved, while the iron is converted into the ferric state (compare Trans., 1907, **91**, 980). In the case of "the lactonic acid," there is also formed a neutral compound having the formula $C_{10}H_{16}O_3$, which was found to be lactonic in character and to contain the group $\vdots C\cdot CO\cdot CH_3$, as it at once yielded iodoform with iodine and alkali; on oxidation, it was converted into terpenylic acid, and was identical with *d*-methoethylheptanonolide, although in certain particulars its properties were not precisely those assigned by Baeyer to that substance.

A comparison of the formula of methoethylheptanonolide (I)



$$\begin{array}{l}CH_3\\CH_3\end{array}\!\!>\!\underset{\displaystyle O}{\underset{|}{C}}\cdot CH\!<\!\begin{array}{l}CH_2\cdot CH_2\\CH_2-\underset{|}{CO}\end{array}\!\!\searrow CO\cdot CH_3$$

I.

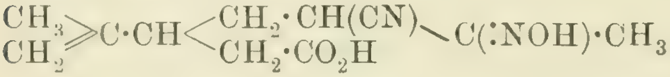


$$\begin{array}{l}CH_3\\CH_2\end{array}\!\!\geqslant\!C\cdot CH\!<\!\begin{array}{l}CH_2\cdot CH(CN)\\CH_2\text{———}CO\end{array}\!\!>\!CH\cdot CH_3$$

II.

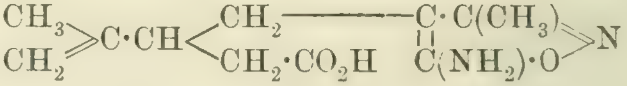
with that of cyanodihydrocarvone (II) shows at once that the process leading from the latter to the former involves scission of the dihydrocarvone ring between the CH and CO groups. This can only be explained by assuming that the attack of the amyl nitrite on the cyanodihydrocarvone was directed at that point and not at the $\cdot CO\cdot CH_2\cdot$ group, as is usually the case when a ketone reacts with an ester in presence of sodium ethoxide.

Experiments with other cyclic ketones containing the group $\colon CH\cdot CO\cdot CH_2\cdot$ have shown us that such is their normal behaviour with nitrous esters; in the cases we have examined, the first product on treatment with water yields an open-chain hydroximino-acid, as when acids are used as catalytic agents. A similar change in the case of cyanodihydrocarvone would lead to the production of the acid having the structure (I):



$$\begin{array}{l}CH_3\\CH_2\end{array}\!\!\geqslant\!C\cdot CH\!<\!\begin{array}{l}CH_2\cdot CH(CN)\\CH_2\cdot CO_2H\end{array}\!\!\searrow C(\colon NOH)\cdot CH_3$$

I.

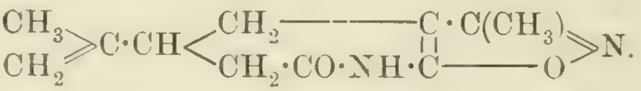


$$\begin{array}{l}CH_3\\CH_2\end{array}\!\!\geqslant\!C\cdot CH\!<\!\begin{array}{l}CH_2\text{————}C\cdot C(CH_3)\\CH_2\cdot CO_2H\quad \overset{||}{C}(NH_2)\cdot O\end{array}\!\!\geqslant N$$

II.

This substance, however, as the oxime of a β-cyanoketone, would readily be converted into an "*iso*oxazolonimide," to which, for reasons which follow, the amino-structure (II) may be adopted.

The free acids here depicted, however, require for their formation the absorption of water; this, however, is absent during the reaction, so that, instead of the free acid, the formula of which has just been given and which represents the amino-acid (*A*), the anhydride or lactam is produced:

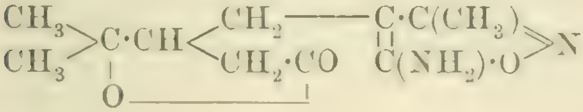


$$\begin{array}{l}CH_3\\CH_2\end{array}\!\!\geqslant\!C\cdot CH\!<\!\begin{array}{l}CH_2\text{————}C\cdot C(CH_3)\\CH_2\cdot CO\cdot NH\cdot \overset{||}{C}\text{———}O\end{array}\!\!\geqslant N.$$

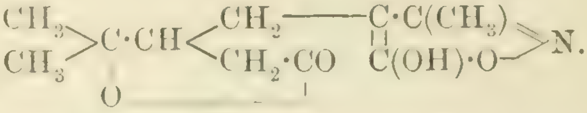
There seems no reason whatever to doubt that this structure fully represents the compound referred to as the lactam (*L*). The very definite acid character of that substance is explained by the presence of the ·NH· group in a ring, and in attachment to an *iso*oxazolone nucleus at a point where a hydroxyl group is known to develop an exceptional acidity.

The formula of the lactam (*L*) thus contains a seven-membered ring in conjunction with a five-membered one, and this is especially interesting in consideration of the ease with which it is formed on heating the amino-acid (*A*).

The mechanism of the formation of the lactonic base (*B*) from the lactam (*L*) can be grasped without difficulty. It is evidently the result of lactone formation in the molecule of the γδ-unsaturated amino-acid, so that the structure of this base is to be represented as (I):

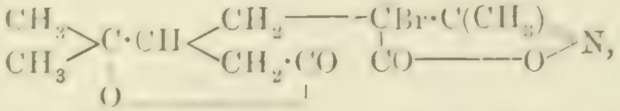


I.



II.

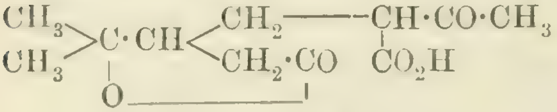
This being the case, hydrolysis of this "*iso*oxazolonimide" should lead to the formation of ammonia and the corresponding *iso*oxazolone (II), and this substance would have all the properties of the compound referred to as "the lactonic acid," but its formula contains the elements of water less than that adopted for this acid in the previous paper. The apparent discrepancy is due only to an obstinate retention of water of crystallisation; for, although we have not obtained the pure anhydrous substance, the crystals of the acid, whilst stable in the atmosphere, if placed over sulphuric acid in a desiccator decompose and are converted in an amorphous mass (compare Trans., 1907, **91**, 989 and 990). To obtain more satisfactory evidence on the point, the action of bromine on the acid was examined, in the anticipation that this would lead to the formation of the neutral monobromo-derivative:

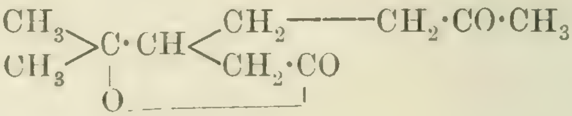


and such was found to be the case. The product was well defined and crystalline, and showed no tendency to unite with water of crystallisation; it was neutral and had the composition indicated. We feel justified therefore in assigning to "the lactonic acid" previously analysed (*loc. cit.*) the formula $C_{11}H_{15}O_4N,H_2O$ and the structure above given.

The characters of the lactonic acid are those of a typical "*iso*oxazolone" or hydroxy*iso*oxazole. That we definitely adopted the hydroxyl rather than the carbonyl formula for the "*iso*oxazolone" residue is because the balance of evidence generally appears in favour of this in the cases previously studied, and also because the amino- and not the imino-structures for the allied acid (*A*) and the lactonic base (*B*) seems to have been definitely established by the experiments already described.

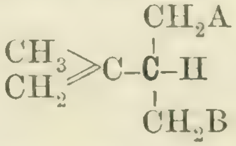
The reduction of the lactonic acid occurs in accordance with the usual behaviour of *iso*oxazolones. We have more recently found that the acid, as well as the compounds from which it is obtained, yields hydroxylamine and methoethylheptanonolide when heated for a considerable time with dilute acids. Doubtless the reaction change consists, in the first instance, of the formation of hydroxylamine and the acid (I), which, being a β-ketonic acid, loses the elements of carbon dioxide with formation of the ketone (II).


I.


II.

It is interesting that the isomeric lactonic base (*B'*), when heated with dilute acid, yields racemic methoethylheptanonolide. This, combined with the fact that the rotatory power previously assigned to the base (*B'*) (*loc. cit.*, p. 987) was very close to that of the base (*B*), led us to re-examine the former, with the result that it was found to be totally inactive, and the rotation given in the first paper was doubtless that of a specimen of the active base (*B*).

The two lactonic bases therefore represent the active and racemic forms respectively, so that the action of mineral acids on the lactam (*L*) leads to a partial inversion of the asymmetric grouping :



$$\begin{array}{c} \mathrm{CH_2A} \\ \big| \\ {}^{\mathrm{CH_3}}_{\mathrm{CH_2}}{>}\mathrm{C{-}C{-}H} \\ \big| \\ \mathrm{CH_2B} \end{array}$$

for active methoethylheptanonolide, in which the unsaturated side-chain is absent, does not racemise under similar and more violent conditions. Thus the group $C{:}CH_2$ functionates in the same way as the carbonyl or cyano-group when attached at the same time as hydrogen to an asymmetric carbon atom.

The constitution of the substance described in the former paper as the isomeric lactam (*L'*) remains obscure. It appears to be an intermediate substance in the formation of the inactive lactonic base (B'), but has a very high dextrorotatory power, $[\alpha]_D$ being greater than +200. It has such characters as might be expected in a stereoisomeride of the lactam (L), but a satisfactory formula indicating this as well as its different optical activity cannot be devised, so that the difference is probably a structural one, but we have no further evidence to cite.

EXPERIMENTAL.

Action of Bromine on the Lactonic Acid.

A solution of bromine in glacial acetic acid was added to one of the lactonic acid in the same solvent, containing excess of sodium acetate. The colour of the halogen at first rapidly disappeared, and when this ceased to be the case the liquid was diluted with water, the solid which separated being collected and purified by crystallisation from alcohol :

0·4112 gave 0·2533 AgBr. Br = 26·21.

$C_{11}H_{16}O_5NBr$ requires Br = 26·25 per cent.

The substance obtained in this way separates from solvents in colourless crystals which melt and decompose at 153°.

The *bromo*-derivative exhibits few of the characteristics of the original compound, being insoluble in alkalis and affording none of the colour reactions so characteristic of the lactonic acid.

Oxidation of the Lactonic Acid.

A solution of the acid in excess of sodium carbonate or hydroxide instantly discharges the colour of potassium permanganate or ferricyanide, and a neutral oxidation product separates. The formation of this compound is not accompanied by that of any compound of low carbon content, so that it may be regarded as certainly containing all the carbon atoms of the original lactonic acid.

The oxidation product appears to be very sensitive to oxidising agents in alkaline media, and is therefore more satisfactorily prepared by the use of solutions of the lactonic acid in dilute sulphuric acid with potassium dichromate as oxidising agent. Quantitative experiments showed that the formation of the compound involves the interaction of one molecule of the lactonic acid and one atom of oxygen.

The substance was purified by crystallisation from alcohol :

0·2731 gave 0·5780 CO_2 and 0·1558 H_2O. C = 57·7 ; H = 6·3.

0·1389 ,, 7·5 c.c. of moist nitrogen at 11° and 768 mm. N = 6·6.

The composition of this substance cannot be expressed by a simple formula, but agrees fairly well with that of a compound of high molecular weight, derived from the lactonic acid by oxidation and subsequent removal of water. The compound having the composition $4(C_{11}H_{17}NO_5 + O) - 7H_2O$ requires $C = 58·0$; $H = 5·9$; $N = 6·2$ per cent. The physical characters of the substance and its almost amorphous structure lend probability to this view.

The oxidation product is insoluble in water, but dissolves sparingly in chloroform, benzene, or ether, and readily in most of the other commonly used organic media.

It is acted on slowly by cold dilute mineral acids, and rapidly when heated with them, giving intensely blue solutions. With concentrated acids, it yields yellow solutions which turn blue when diluted with water. These blue solutions turn yellow on addition of excess of alkali, but when re-acidified they gradually regain the original blue colour.

Action of Sodium Hydroxide and Ferrous Hydroxide on the Lactonic Acid.

When a solution of the sodium salt of the lactonic acid in excess of alkali is shaken with freshly precipitated ferrous hydroxide, the green colour of the latter gradually disappears, while the odour of ammonia is almost at once made perceptible. In order to obtain the reduction products, 18 grams of the acid were dissolved in 600 c.c. of *N*-sodium hydroxide, and to this was then added 36 grams of ferrous chloride dissolved in about 350 c.c. of water, the whole being heated to boiling until the odour of ammonia was no longer perceptible, a process which required about one hour. The iron hydroxides were then removed by filtration, extracted repeatedly with boiling water, and the united filtrates evaporated to 200 c.c., cooled, mixed with 30 c.c. of concentrated hydrochloric acid, and extracted with benzene. The latter, on evaporation, left an oil which finally set to a hard, crystalline mass, weighing 13·2 grams, or 96 per cent. of the calculated amount:

0·3350 gave 0·7978 CO_2 and 0·2594 H_2O. $C = 64·9$; $H = 8·6$.

$C_{10}H_{16}O_3$ requires $C = 65·2$; $H = 8·7$ per cent.

The substance crystallised from water in needles or plates melting at 47—48°, and boiled without decomposition about 300°.

0·5252, made up to 20 c.c. with absolute alcohol at 15°, gave a rotation of $+3·10°$, whence $[\alpha]_D^t$ $+59·0$.

It was neutral to litmus, but exhibited the lactonic character of the acid from which it had been prepared. 0·3939 gram, after boiling with 25 c.c. 0·98 *N*-sodium hydroxide, partly neutralised the latter, so that after fifteen minutes only 3·4 c.c. *N*/10-sulphuric acid were required for neutralisation. The equivalent found was 187, that required for a lactone, $C_{10}H_{16}O_3$, being 184.

The substance was also ketonic in character, yielding precipitates with solutions of phenylhydrazine acetate and semicarbazide acetate, and also iodoform on treatment with iodine and alkali, indicating that it contained the ketonic group $:C\cdot CO\cdot CH_3$.

Baeyer has described a substance having the above formula, and which also contains the groupings shown to be present in the substance here under notice. Baeyer's compound was obtained by oxidising trihydroxyterpan (*Ber.*, 1898, **31**, 3216), and it was assigned the melting point 48—49°, but the rotation of its 13 per cent. alcoholic solution corresponded with $[\alpha]_D +44\cdot4°$. The substance was methoethylheptanonolide, which has also been described by Jodlerowski (*Chem. Centr.*, 1899, i, 1241), according to whom the melting point is 45—46° and $[\alpha]_D +55\cdot3°$ in alcoholic solution.

In view of these discrepancies, we undertook the oxidation of the substance obtained by us, employing the method used by Wallach (*Annalen*, 1893, **277**, 118). From 2 grams of the methyl ketone, 1·87 grams of an acid were obtained, which melted at 57° in the hydrated condition and at 90° when anhydrous, was inactive, and had all the properties of terpenylic acid:

0·3798 gave 0·7002 CO_2 and 0·2531 H_2O. C = 50·3; H = 7·4.

$C_8H_{12}O_4,H_2O$ requires C = 50·6; H = 7·4 per cent.

The substance obtained by reducing the lactonic acid is therefore undoubtedly methoethylheptanonolide. In all probability, it is thus isolated in a high state of purity, and possibly the low rotatory power observed by Baeyer (*loc. cit.*) was due to the presence of some quantity of the inactive ketone in his specimen.

Formation of d-*Methoethylheptanonolide by the Action of Acids on the Lactonic Base* (B).

During the preparation of the lactonic acid from the lactonic base (*B*) (Trans., 1907, **91**, 989), indications of the occurrence of a secondary reaction were frequently obtained, a slow evolution of carbon dioxide being observed; moreover, the yield of lactonic acid never exceeded about 50 per cent. of that theoretically possible, and the mother liquor invariably showed powerful reducing properties similar to those of a solution of hydroxylamine. The presence of the latter substance was finally established by converting it into impure acetoxime with acetone and alkali, hydrolysing the extracted oxime with hydrochloric acid, and thus obtaining hydroxylamine hydrochloride free from organic matter.

In purifying the mother liquor for the above purpose, it was noticed that, when it was shaken with benzene, a further separation of the lactonic acid took place, and on examining the benzene extract the latter was found to yield an oil which slowly crystallised; the product thus obtained was found to be *d*-methoethylheptanonolide in a state approaching purity. After the complete removal of this substance, extraction of the mother liquor with chloroform leads to the recovery of a further quantity of the lactonic acid.

In this way, from 36 grams of the lactonic base, 22 grams of the lactonic acid and 7·4 grams of the methyl ketone were obtained, representing 80 per cent. of the theoretical amount.

Formation of Racemic Methoethylheptanonolide by the Action of Dilute Acids on the Racemic Isomeric Lactonic Base (B′).*

In the hope of throwing light on the question of the relation between the bases (*B*) and (*B′*) (Trans., 1907, **91**, 985 and 987), the hydrolysis of the latter was undertaken. The substance was heated for five hours with about fifteen times its weight of *N*-sulphuric acid, and afterwards with excess of sodium hydroxide and ferrous hydroxide until ammonia ceased to be evolved. The filtered and evaporated solution was then acidified and extracted with chloroform, which removed a considerable quantity of an oil. This rapidly solidified on cooling, and the resulting material was crystallised from ether, from which it separated in colourless needles melting at 63°. It was optically inactive, and was identical in all respects with the *d*-methoethylheptanonolide described by Tiemann and Semmler (*Ber.*, 1895, **28**, 1778).

Benzylidene Derivative of the Base (B).

Equimolecular proportions of the lactonic base (*B*) (Trans., 1907, **91**, 985) and benzaldehyde were treated together on the water-bath for three hours. The product when cool became crystalline on trituration with alcohol, and was purified by repeated crystallisation from that solvent:

0·2958 gave 23·8 c.c. moist nitrogen at 18° and 756 mm. N = 9·2.

$C_{18}H_{20}O_3N_2$ requires N = 9·0 per cent.

The compound crystallises from alcohol in almost colourless crystals, which melt at 120°, forming a yellow liquid. It dissolves somewhat readily in benzene, acetone, chloroform, or acetic acid, more sparingly in ether, carbon tetrachloride, carbon disulphide, or cold alcohol. It is insoluble in dilute acids or alkalis. When boiled with water, especially in presence of acids, it is resolved into its components.

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* This substance was previously stated to be active (compare p. 1922).

CLXXXVII.—*The Synthesis of Acridines and Phenonaphthacridines: Tetra- and Hexa-methylacridines: Dimethylphenonaphthacridines: Dixylylmethylenediamines.*

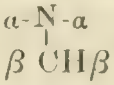
By ALFRED SENIER and ARTHUR COMPTON.

HITHERTO the simplest acridine obtained by the condensation of methylene chloride with arylamines was hexamethylacridine. The extension of this method to the synthesis of simpler acridines seemed possible, although the reaction had already been studied by several investigators. (For references, compare Senier and Goodwin, Trans., 1902, **81**, 280.) With this object in view, we re-investigated the reaction between methylene chloride and the xylidines, and succeeded in obtaining two tetramethylacridines. Eventually the scope of our enquiry widened into a more general study of the synthesis of acridines and phenonaphthacridines. The following methods of synthesis were employed:

1. Condensation of aryl- or naphthyl-amines or mixtures of them with methylene di-iodide (Senier and Goodwin, *loc. cit.*), or methylene dichloride (Senier and Austin, Trans., 1906, **89**, 1390).

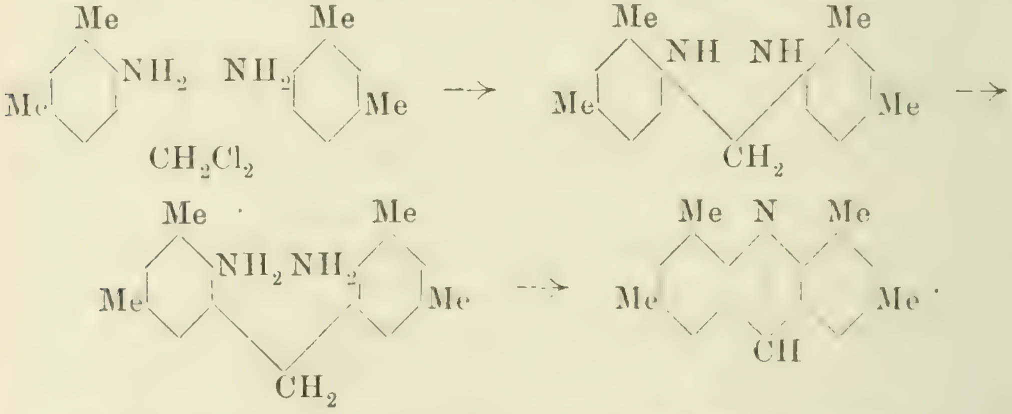
2. Condensation of mixtures of arylamines and phenols or naphthols with methylene di-iodide (Senier and Austin, Trans., 1907, **91**, 1240), or methylene dichloride.

3. Condensation of diarylmethylenediamines with an arylamine and its hydrochloride (Ullmann and Waitz, *Ber.*, 1903, **36**, 1019).

From *m*-4-xylidine and *p*-xylidine and the analogous xylenols by the above methods, we obtained the corresponding dixylylmethylenediamines and tetramethylacridines. *p*-Xylidine gave a diamine, but no acridine by the first method; but the desired acridine was obtained from the diamine by the third and also by the second method from the xylidine and xylenol. Improvements were made in the preparation of 1:3:4:6:7:9-hexamethylacridine (Senier and Goodwin, *loc. cit.*) by the first method, using methylene di-iodide, and it was found that by means of methylene dichloride the same base could be prepared. α- and β-Naphthols with each of the xylidines gave by the second method the corresponding dimethylphenonaphthacridines, one of which Ullmann (*Chem. Centr.*, 1901, **2**, 568) has already described as the result of the interaction of formaldehyde and a mixture of xylidine and naphthol. The experiments of Senier and Austin (*loc. cit.*) showed that the first method was not a promising one for the preparation of phenonaphthacridines, and it was therefore not used. Further, we found that the xylenol and naphthylamine could not replace the naphthol and xylidine, for, in an experiment using *m*-4-xylenol and α naphthylamine only,  $\overset{\alpha\text{-N-}\alpha}{\underset{\beta\ \text{CH}\beta}{|}}$-dinaphthacridine was obtained.

The inability of *p*-xylidine to condense directly to an acridine by the first method, in spite of repeated attempts to effect the reaction, appears to be due to the absence of a methyl group in the para-position with respect to the amino-group. For, excluding the alkyl substitution in the meso-position, every alkyl derivative of acridine hitherto discovered by the first method, or by the analogous method in which formaldehyde is used, contains an alkyl in a para-position with respect to the nitrogen linking. Further, if it be assumed that by the method referred to a methylenediamine is first formed (with or without an intermediate methylenearylamine), it may well undergo the methylenebenzidine metastasis observed in the case of toluidines by Eberhardt and Welter (*Ber.*, 1894, **27**, 1804) before the final condensation to acridine takes place. In this event, only those arylamines which contain alkyl groups in para-positions with respect to their amino-groups can form such methylenediamines as are capable of being metastasised into diaminodiarylmethanes in which the amino-groups arrange themselves in an ortho-position with respect to the methylene-group. In all other cases, the formation of acridines is excluded, since by the benzidine metastasis, *pp*-diaminodiarylmethanes would be formed.

Thus, in the case of *m*-4-xylidine, the course of the changes would be :



That diaminodiarylmethanes are formed when formaldehyde or one of its analogues is used, and that they condense to acridines, is shown by the experiments of Meyer and Gross (*Ber.*, 1899, **32**, 2352), Ullmann and Marić (*Ber.*, 1901, **34**, 4307), Haase (*Ber.*, 1903, **36**, 588), and Ullmann (*Ber.*, 1903, **36**, 1017).

The third method was used by Ullmann and Waitz in the preparation of 3 : 7-dimethylacridine from di-*p*-tolylmethylenediamine and a mixture of *p*-toluidine and its hydrochloride. The reaction is closely related to the third one described by Ullmann and Naef (*Ber.*, 1900, **33**, 906). That by the first method, *m*-4-xylidine yields an acridine, whilst *p*-xylidine does not, we have explained by the metastasis which the intermediate diamines formed undergo. Now by the third method, in which the starting point is the diamine, that the diamines derived from both xylidines yield acridines, indicates that when this method is made use of no metastasis take place; for, whilst the diaminodiarylmethane derived by metastasis from the 1 : 3 : 4-diamine might give an acridine by this method, the corresponding compound from the 1 : 4 : 5-diamine could not do so. In both cases, therefore, it is probable that substitution with condensation takes place directly between the arylamine and the methylenediamine.

1. *Condensation of m-4-Xylidine with Methylene Dichloride.*

When *m*-4-xylidine (2 mols.) and methylene dichloride (1 mol.) are heated in a closed tube at 160—170° for three hours, or at a somewhat higher temperature for a shorter period, the chief product is the corresponding dixylylmethylenediamine, identical with that described by Senier and Goodwin (Trans., 1902, **81**, 284) as the result of the interaction of commercial xylidine and methylene di-iodide. When, however, a higher temperature is employed, the tube being heated at once to 270—290°, no diamine can be detected, but, instead, a small yield of 1 : 3 : 7 : 9-tetramethylacridine is obtained. The mesophenyl derivative of this base was prepared by Ullmann and Weintraub from the xylidine by the action of benzaldehyde (*Ber.*, 1903, **36**, 1021).

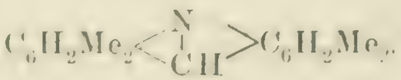
1 : 3 : 4-*Dixylylmethylenediamine*, $CH_2(NH \cdot C_6H_3Me_2)_2$ (*Senier and Goodwin*).

The semicrystalline contents of the tube were heated with methylated spirit, containing a small proportion of potassium hydroxide, and the clear solution obtained was allowed to cool, when small, yellow needles separated, which were collected and washed successively with water and methylated spirit, and finally recrystallised from the latter solvent several times. The base consists of almost colourless needles, which melt at 128° (corr.). On analysis:

0·2253 gave 21·6 c.c. moist nitrogen at 14·2° and 754 mm. N = 11·18.

$C_{17}H_{22}N_2$ requires N = 11·02 per cent.

1 : 3 : 7 : 9-*Tetramethylacridine*,



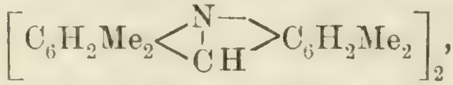
$$C_6H_2Me_2<\overset{N}{\underset{CH}{|}}>C_6H_2Me_2.$$

The tube containing the xylidine and methylene dichloride was heated at once to 270—290° and kept at that temperature one and a-half to two hours. Towards the close of the heating, a yellow sublimate usually collected at the cooler end of the tube. The contents were treated with cold ethyl acetate or acetone, and the dark brown powder remaining was dissolved in hot dilute hydrochloric acid, which solution on cooling deposited golden-brown needles. The crystals were collected, treated with concentrated ammonium hydroxide solution, and washed with water. The base thus obtained, consisting of a white powder, was dissolved in hot methylated spirit, which on cooling yielded long, pale yellow, silky needles. After several recrystallisations, crystals were obtained which melted constantly at 122° (corr.). 1 : 3 : 7 : 9-*Tetramethylacridine* is also very soluble in cold ether or chloroform, less so in cold acetone, benzene, or pyridine. Its solution in methylated spirit shows faint blue fluorescence. On analysis :

0·1532 gave 0·4871 CO_2 and 0·1016 H_2O. C = 86·71 ; H = 7·37.

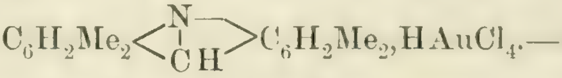
0·1915 ,, 9·8 c.c. moist nitrogen at 14·5° and 752 mm. N = 5·94.

$C_{17}H_{17}N$ requires C = 86·81 ; H = 7·23 ; N = 5·96 per cent.

Platinichloride,  $\left[C_6H_2Me_2<\begin{smallmatrix}N\\|\\CH\end{smallmatrix}>C_6H_2Me_2\right]_2,H_2PtCl_6$.—Orange-brown crystals of this compound were obtained by adding a few drops of concentrated platinic chloride solution to a solution of the base in methylated spirit. The crystals were washed with ether and dried at 105°. The compound crystallises readily from a mixture of equal volumes of glacial acetic and concentrated hydrochloric acids. On analysis :

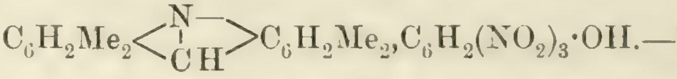
0·0418 gave 0·0092 Pt. Pt = 22·01.

$C_{34}H_{36}N_2Cl_6Pt$ requires Pt = 22·14 per cent.

Aurichloride,  $C_6H_2Me_2<\begin{smallmatrix}N\\|\\CH\end{smallmatrix}>C_6H_2Me_2,HAuCl_4$.—A few drops of a solution of gold chloride were added to a solution of the base in a mixture of concentrated hydrochloric and glacial acetic acids, when a yellow precipitate separated. This was collected, washed with ether, and dried at 105°. On analysis :

0·0528 gave 0·0180 Au. Au = 34·09.

$C_{17}H_{18}NCl_4Au$ requires Au = 34·28 per cent.

Picrate,  $C_6H_2Me_2<\begin{smallmatrix}N\\|\\CH\end{smallmatrix}>C_6H_2Me_2,C_6H_2(NO_2)_3\cdot OH$.—This salt was obtained by adding a hot solution of picric acid in methylated spirit to a hot solution of the base in the same solvent. Yellowish-brown, glistening crystals separated on cooling, which were collected, washed with methylated spirit, recrystallised from benzene, and dried at 110°. They melted at 210—211° (uncorr.). On analysis :

0·1699 gave 17·4 c.c. moist nitrogen at 16° and 758 mm. N = 11·91.

$C_{23}H_{20}O_7N_4$ requires N = 12·07 per cent.

2. *Condensation of a Mixture of* m-4-*Xylidine and* m-4-*Xylenol with Methylene Dichloride*: 1 : 3 : 7 : 9-*Tetramethylacridine.*

1 : 3 : 7 : 9-Tetramethylacridine is readily obtained by this method, and the yield is better than by that just described. m-4-Xylidine (1 mol.), m-4-xylenol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube at 270—290° for two hours. The contents of the tube were treated with cold acetone or ethyl acetate and the insoluble portion was crystallised from dilute hydrochloric acid, the resulting hydrochloride decomposed with ammonium hydroxide, and the base recrystallised twice from methylated spirit. Some ammonium hydroxide was added to the solution in methylated spirit before the first recrystallisation, but not enough to cause a turbidity, in order to ensure complete decomposition of the salt. The crystals were finally washed with water and crystallised again from dilute spirit. They melted as before at 122° (corr.). On analysis:

0·0804 gave 0·2555 CO_2 and 0·0535 H_2O. C = 86·67 ; H = 7·39.
0·1040 ,, 5·2 c.c. moist nitrogen at 16·5° and 756 mm. N = 5·78.
$C_{17}H_{17}N$ requires C = 86·81 ; H = 7·23 ; N = 5·96 per cent.

3. *Condensation of a Mixture of* m-4-*Xylidine and* m-4-*Xylenol with Methylene Di-iodide*: 1 : 3 : 7 : 9-*Tetramethylacridine.*

An experiment was made with *m*-4-xylidine, xylenol, and methylene-di-iodide, which, on account of the high boiling point of the di-iodide, could be performed in an open vessel. The dark brown liquid which resulted was treated in a similar manner to that described above for the contents of the closed tubes. The crystals obtained had the same melting point, and were identical in appearance with 1 : 3 : 7 : 9-tetramethylacridine.

4. *Condensation of* p-*Xylidine with Methylene Dichloride.*

With *p*-xylidine, the corresponding methylenediamine was obtained readily, but, although repeated attempts were made even at temperatures of 300° and upwards, we did not succeed in isolating the corresponding tetramethylacridine. The base was obtained, however, by other methods.

1 : 4 : 5-*Dixylylmethylenediamine*, $CH_2(NH\cdot C_6H_3Me_2)_2$.

p-Xylidine (2 mols.) and methylene dichloride (rather more than 1 mol.) were heated in a closed tube for two and a-half hours at

160—170°. The contents of the tube were dissolved in hot methylated spirit, and the solution was precipitated by a solution of potassium hydroxide. The precipitate was washed with water, dried, and recrystallised twice from light petroleum. The base consists of pale brown needles, which soften at 135° and melt at 138°. It is very soluble in chloroform, benzene, light petroleum, alcohol, or glacial acetic acid, but less so in ether. On analysis:

0·3114 gave 0·9175 CO_2 and 0·2447 H_2O. C = 80·35 ; H = 8·73.
0·2456 ,, 23·4 c.c. moist nitrogen at 17° and 756 mm. N = 11·00.
$C_{17}H_{22}N_2$ requires C = 80·31 ; H = 8·66 ; N = 11·02 per cent.

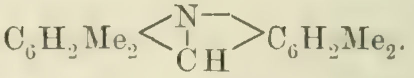
Platinichloride, $CH_2(NH\cdot C_6H_3Me_2)_2,H_2PtCl_6,H_2O$.—A solution of platinic chloride was added to a solution of the base in methylated spirit containing a small proportion of hydrochloric acid. The yellow, crystalline precipitate obtained was washed with ether and dried at 110°. On analysis:

0·1063 gave 0·0303 Pt. Pt = 28·50.
$C_{17}H_{26}ON_2Cl_6Pt$ requires Pt = 28·57 per cent.

5. *Condensation of a Mixture of* p-*Xylidine and* p-*Xylenol with Methylene Dichloride.*

When *p*-xylidine and xylenol are gradually heated in a closed tube with methylene dichloride to 250—270°, the xylenol takes no part in the reaction and 1 : 4 : 5-dixylylmethylenediamine, described above, is formed. The diamine was identified by its melting point, solubility, and appearance. A different result is obtained if the tube is heated rapidly to about 300° or upwards, when acridine condensation is brought about.

1 : 4 : 6 : 9-*Tetramethylacridine*,



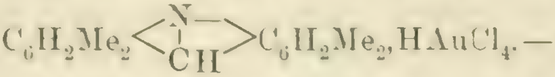
$C_6H_2Me_2{<}\overset{N—}{\underset{CH}{|}}{>}C_6H_2Me_2$.

p-Xylidine (1 mol.), *p*-xylenol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube rapidly to 270° and then the temperature was gradually increased to about 350°. The entire heating lasted from two to two and a half hours, the highest temperature being maintained for nearly an hour. The contents of the tube could not be separated by means of acetone, as was done in the case of the isomeride above described. They were dissolved in warm methylated spirit, giving a solution with reddish-green fluorescence. This solution was precipitated by a concentrated solution of potassium hydroxide, and the resulting pale brown powder was collected, dried, and then distilled under reduced pressure. A yellow, crystalline sublimate was obtained, which, after being recrystallised twice from methylated spirit and finally from ethyl acetate, consisted of greenish-yellow needles which melted at 179·5—180·5° (corr.). The base is also very soluble in ether, chloroform, or benzene, less so in acetone, pyridine, or light petroleum. The pure base dissolved in methylated spirit exhibits a pale blue fluorescence. On analysis :

0·1926 gave 0·6110 CO_2 and 0·1314 H_2O. C = 86·52 ; H = 7·58.

0·2010 ,, 9·4 c.c. moist nitrogen at 15·5° and 774 mm. N = 5·57.

$C_{17}H_{17}N$ requires C = 86·81 ; H = 7·23 ; N = 5·96 per cent.

Aurichloride,  $C_6H_2Me_2<\overset{N—}{\underset{CH}{|}}>C_6H_2Me_2,HAuCl_4$.—A few drops of solution of gold chloride were added to a solution of the base in methylated spirit with which a small proportion of hydrochloric acid had been mixed. An orange precipitate formed immediately, which was washed with methylated spirit and dried at 105°. On analysis :

0·0722 gave 0·0247 Au. Au = 34·21.

$C_{17}H_{18}NCl_4Au$ requires Au = 34·28 per cent.

6. *Condensation of Dixylylmethylenediamines with Xylidines and Xylidine Hydrochlorides:* 1 : 3 : 7 : 9- *and* 1 : 4 : 6 : 9-*Tetramethylacridines*

1 : 3 : 4-Dixylylmethylenediamine (1 mol.), *m*-4-xylidine (1 mol.), and its hydrochloride (1 mol.) were heated in a closed tube for two hours at 270—300°. The semi-solid, green mass in the tube was extracted with cold acetone and the green, fluorescent solution was precipitated by pouring it into water. A yellow precipitate was obtained, which was boiled for a few minutes with a solution of potassium hydroxide in methylated spirit, washed with water, and recrystallised several times from methylated spirit. The resulting base proved to be identical in melting point, solubility, and crystalline appearance with 1 : 3 : 7 : 9-tetramethylacridine. The *aurichloride* was prepared, and on analysis :

0·0682 gave 0·0235 Au. Au = 34·45.

$C_{17}H_{18}NCl_4Au$ requires Au = 34·28 per cent.

1 : 4 : 5-Dixylylmethylenediamine, heated in a similar manner to 250—270° with *p*-xylidine and its hydrochloride, gave a black mass, which was dissolved in methylated spirit, the solution precipitated by solution of potassium hydroxide, collected, dried, and distilled under reduced pressure. The semicrystalline distillate was washed with acetone and recrystallised from methylated spirit containing a little ammonium hydroxide. From its melting point, solubility, appearance, and behaviour when distilled, the base was identified as 1 : 4 : 6 : 9-tetramethylacridine. The *aurichloride* was prepared, and on analysis :

0·0639 gave 0·0218 Au. Au = 34·22.

$C_{17}H_{18}NCl_4Au$ requires Au = 34·28 per cent.

7. *Condensation of ψ-Cumidine with Methylene Dichloride:* 1 : 3 : 4 : 6 : 7 : 9-*Hexamethylacridine* (*Senier and Goodwin*).

ψ-Cumidine (2 mols.) and methylene dichloride (1 mol.) were heated in a closed tube at 210—240° for three hours. The contents of the tube were washed by adding a mixture of methylated spirit and a solution of potassium hydroxide, heating the whole to boiling, and then setting aside to cool. The insoluble residue was then washed carefully with cold acetone, the harder portions being rubbed in a mortar with the solvent. After this treatment, a few crystallisations from ethyl acetate, benzene, or glacial acetic acid gave the base in a state of purity, melting at 217° (222° corr.), the same as found by Senier and Goodwin. On analysis:

0·2464 gave 0·7814 CO_2 and 0·1752 H_2O. C = 86·49; H = 7·90.

$C_{19}H_{21}N$ requires C = 86·69; H = 7·98 per cent.

8. *Condensation of ψ-Cumidine and Methylene Di-iodide:* 1 : 3 : 4 : 6 : 7 : 9-*Hexamethylacridine* (*Senier and Goodwin*).

Mr. P. C. Austin, in the course of experiments in which he had frequently to prepare hexamethylacridine, discovered some useful modifications of the original method for its preparation, and working under certain conditions he noticed the formation of an interesting intermediate compound which is probably di-ψ-cumylmethylenediamine.

Mr. Austin finds that alkali, either as carbonate or hydroxide, may be omitted in the preparation of the base, and that, if small quantities are desired, the operation can be conducted in a few minutes over the open flame in a test-tube without any danger of over-heating; 2—3 grams of ψ-cumidine are melted, a few drops of methylene di-iodide added, and the mixture warmed until the reaction begins. As soon as the first violence has subsided, the remainder of the methylene di-iodide is added, and the liquid is boiled for one or two minutes. After cooling, the mass is heated to boiling with a solution of potassium hydroxide in methylated spirit, and from the clear solution, on cooling, greenish-yellow crystals of hexamethylacridine are obtained at once.

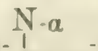
The colourless compound, di-ψ-cumylmethylenediamine, was obtained, for example, in the following experiment. ψ-Cumidine (12 grams), methylene di-iodide (9 grams), and potassium hydroxide (10 grams) were heated together to 190° in an oil-bath, using a reflux condenser. As soon as the reaction began, the flask was cooled for a few minutes, after which, when it became more moderate, the heating was resumed and continued for several hours. After cooling, the contents of the flask were boiled with water to remove the alkali, the residue was then washed with water and with a little cold acetone, and finally extracted by boiling with acetone. From the clear solution, colourless crystals were obtained on standing. They are very soluble in ether, carbon disulphide, chloroform, acetone, ethyl acetate, benzene, or glacial acetic acid, but less so in alcohol. The solutions exhibit no fluorescence. This compound is probably *di-ψ-cumylmethylenediamine*, $CH_2(NH{\cdot}C_6H_2Me_3)_2$. A *platinichloride* was prepared. On analysis:

0·1233 gave 0·0336 Pt. Pt = 27·25.

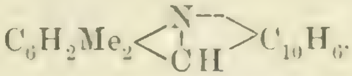
$C_{19}H_{28}N_2Cl_6Pt,H_2O$ requires Pt = 27·46 per cent.

This compound was at first thought to be a hydro-derivative of hexamethylacridine, especially as by treatment with bromine in a benzene solution hexamethylacridine was formed, but no hydro-derivative of the latter could be obtained by reduction. The compound will be further examined, but meanwhile it may be noted that its hydrochloride, which forms gradually, is nearly colourless, its platinichloride is yellow, its solutions are not fluorescent, and it is easily soluble in either ethyl acetate or acetone; whilst hexamethylacridine hydrochloride is red and forms immediately, its platinichloride is scarlet, its solutions are fluorescent, and it is not easily soluble in either ethyl acetate or acetone.

9. *Condensation of m-4-Xylidine and α-Naphthol with Methylene Dichloride: 9:11-Dimethylpheno-*$\overset{N\text{-}\alpha}{\underset{CH\beta}{|}}$*-naphthacridine,* $C_6H_2Me_2<\overset{N}{\underset{CH}{|}}>C_{10}H_6$.



$\overset{N\text{-}\alpha}{\underset{CH\beta}{|}}$



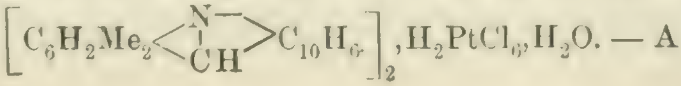
$C_6H_2Me_2<\overset{N}{\underset{CH}{|}}>C_{10}H_6$

m-4-Xylidine (1 mol.), α-naphthol (1 mol.), and methylene dichloride (1 mol.) were heated for two hours in a closed tube at 250—260°. The dark red, viscous mass, after cooling, was first well washed with acetone. The deep yellow residue was then boiled for a few minutes with methylated spirit to which a small proportion of a solution of potassium hydroxide had been added, and the mixture was set aside to cool. The residue which remained was washed with water and also with methylated spirit, and then dissolved in amyl alcohol, from which solvent it was crystallised several times. Light petroleum or glacial acetic acid were also used in some experiments as media for recrystallisation. The base forms small, yellow, glistening crystals which melt at 155° (corr.). It is very soluble also in benzene, toluene, or chloroform. In solution in amyl alcohol, it shows a blue, and in glacial acetic acid a green, fluorescence. On analysis:

0·1656 gave 0·5377 CO_2 and 0·0910 H_2O. C = 88·55; H = 6·10.

0·1713 ,, 8 c.c. moist nitrogen at 13° and 756 mm. N = 5·49.

$C_{19}H_{15}N$ requires C = 88·71; H = 5·84; N = 5·45 per cent.



Platinichloride, $\left[C_6H_2Me_2<\overset{N}{\underset{CH}{|}}>C_{10}H_6\right]_2,H_2PtCl_6,H_2O$. — A few drops of a concentrated solution of platinic chloride were added to a solution of the base in a mixture of concentrated hydrochloric and glacial acetic acids. The yellow precipitate which formed was washed with light petroleum and dried at 110°. On analysis:

0·0526 gave 0·0109 Pt. Pt = 20·72.

$C_{38}H_{34}ON_2Cl_6Pt$ requires Pt = 20·70 per cent.

10. *Condensation of* m-4-*Xylidine and* α-*Naphthol with Methylene Di-iodide*: 9 : 11-*Dimethylpheno*-$\overset{N\text{-}\alpha}{\underset{CH\beta}{|}}$-*naphthacridine.*

The xylidine, naphthol, and methylene di-iodide were used in molecular proportions. The xylidine and naphthol were heated to boiling in an open vessel, and the methylene di-iodide was added in small portions at a time. The heating was continued until the somewhat vigorous reaction was completed, and the resulting mass was treated in the manner just described (9). By their melting point, solubilities, and appearance, the crystals obtained were identified as 9 : 11-dimethylpheno-$\overset{N\text{-}\alpha}{\underset{CH\beta}{|}}$-naphthacridine.

11. *Condensation of* m-4-*Xylidine and* β-*Naphthol with Methylene Dichloride*: 9 : 11-*Dimethylpheno*-$\overset{N\text{-}\beta}{\underset{CH\alpha}{|}}$-*naphthacridine* (*Ullmann*).

m-4-Xylidine (1 mol.), β-naphthol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube and the contents treated as in the preparation of the α-isomeride (9), except that, instead of recrystallising from amyl alcohol, the product, which was pale yellow, was dissolved in methylated spirit, precipitated therefrom with ammonium hydroxide, and the precipitate washed with water and recrystallised from methylated spirit. The final crystallisation may also be effected from amyl alcohol. In solution in methylated spirit, the base exhibits a blue fluorescence. It melts at 153° (corr.), and is identical with that described by Ullmann (*loc. cit.*). On analysis:

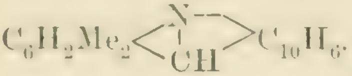
0·1578 gave 0·5135 CO_2 and 0·0860 H_2O. C = 88·74; H = 6·05.

$C_{19}H_{15}N$ requires C = 88·71; H = 5·84 per cent.

12. *Condensation of* m-4-*Xylidine and* β-*Naphthol with Methylene Di-iodide*: 9 : 11-*Dimethylpheno*-$\overset{N\text{-}\beta}{\underset{CH\alpha}{|}}$-*naphthacridine* (*Ullmann*).

Substituting methylene di-iodide in the experiment just described for the dichloride, the same base is obtained. The operation is conducted as in (10) in an open vessel.

13. *Condensation of* p-*Xylidine and α-Naphthol with Methylene Dichloride: 8:11-Dimethylpheno*$\overset{\mathrm{N}\text{-}\alpha}{\underset{\mathrm{CH}\beta}{|}}$*-naphthacridine*,



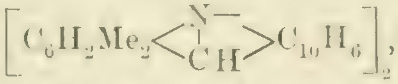
$$\mathrm{C_6H_2Me_2}{<}\overset{\mathrm{N}—}{\underset{\mathrm{CH}}{|}}{>}\mathrm{C_{10}H_6}.$$

p-Xylidine (1 mol.), α-naphthol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube to the same degree as in the corresponding experiment with *m*-4-xylidine (9). The contents of the tube were treated also in the same manner, and the recrystallisation was effected from amyl alcohol with final washing with methylated spirit.

The base consists of dull green needles which melt at 122·5° (corr.). It is soluble in acetone, benzene, or glacial acetic acid, less so in methylated spirit, light petroleum, or amyl alcohol. Its solution in methylated spirit shows blue fluorescence. On analysis:

0·1410 gave 0·4583 CO_2 and 0·0764 H_2O. $C = 88·65$; $H = 6·02$.
0·1402 ,, 6·6 c.c. moist nitrogen at 16·8° and 756 mm. $N = 5·44$.
$C_{19}H_{15}N$ requires $C = 88·71$; $H = 5·84$; $N = 5·45$ per cent.

Platinichloride,

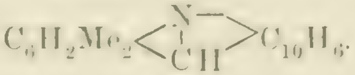


$$\left[\mathrm{C_6H_2Me_2}{<}\overset{\mathrm{N}—}{\underset{\mathrm{CH}}{|}}{>}\mathrm{C_{10}H_6}\right]_2,\mathrm{H_2PtCl_6,H_2O}.$$

— To the base dissolved in glacial acetic acid, containing a small proportion of hydrochloric acid, a few drops of a concentrated solution of platinic chloride were added. The salt separated on standing as a yellow precipitate, which was washed with glacial acetic acid, then with light petroleum, and dried at 100°. On analysis:

0·0302 gave 0·0063 Pt. Pt = 20·86.
$C_{38}H_{34}ON_2Cl_6Pt$ requires Pt = 20·70 per cent.

14. *Condensation of* p-*Xylidine and β Naphthol with Methylene Dichloride: 8:11 Dimethyl* $\overset{\mathrm{N}\text{-}\beta}{\underset{\mathrm{CH}\alpha}{|}}$ *-naphthacridine*,



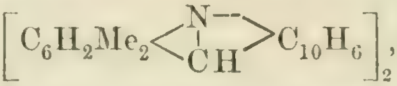
$$\mathrm{C_6H_2Me_2}{<}\overset{\mathrm{N}—}{\underset{\mathrm{CH}}{|}}{>}\mathrm{C_{10}H_6}.$$

This base was obtained, using equal molecular proportions of *p*-xylidine, β naphthol, and methylene dichloride, in the same manner as in the preparation of the α-isomeride (13) just described, except that the final recrystallisations were effected from methylated spirit. It consists of small, well-formed, pale yellow, glistening needles which melt at 154° (corr.). It is very soluble in benzene, toluene, light petroleum, or glacial acetic acid. Its solution in methylated spirit exhibits faint blue fluorescence. On analysis:

0·1570 gave 0·5099 CO_2 and 0·0872 H_2O. C = 88·57; H = 6·17.

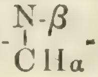
0·1396 ,, 6·8 c.c. moist nitrogen at 17° and 764 mm. N = 5·68.

$C_{19}H_{15}N$ requires C = 88·71; H = 5·84; N = 5·45 per cent.

Platinichloride,  $\left[C_6H_2Me_2<\overset{N--}{\underset{CH}{|}}>C_{10}H_6\right]_2,H_2PtCl_6,(H_2O)_2$.—The base was dissolved in a mixture of glacial acetic and concentrated hydrochloric acids, and to this platinic chloride solution was added. The yellow precipitate, which formed at once, was washed with light petroleum and dried at 115°. On analysis:

0·1284 gave 0·0261 Pt. Pt = 20·32.

$C_{28}H_{36}O_2N_2Cl_6Pt$ requires Pt = 20·31 per cent.

15. *Condensation of* p-*Xylidine and β-Naphthol with Methylene Di-iodide: 8 : 11-Dimethyl-*  $\overset{N\text{-}\beta}{\underset{CH\,\alpha}{|}}$ *-naphthacridine.*

The same base was obtained by heating together as in (10) and (12), in an open vessel, β-naphthol and methylene di-iodide.

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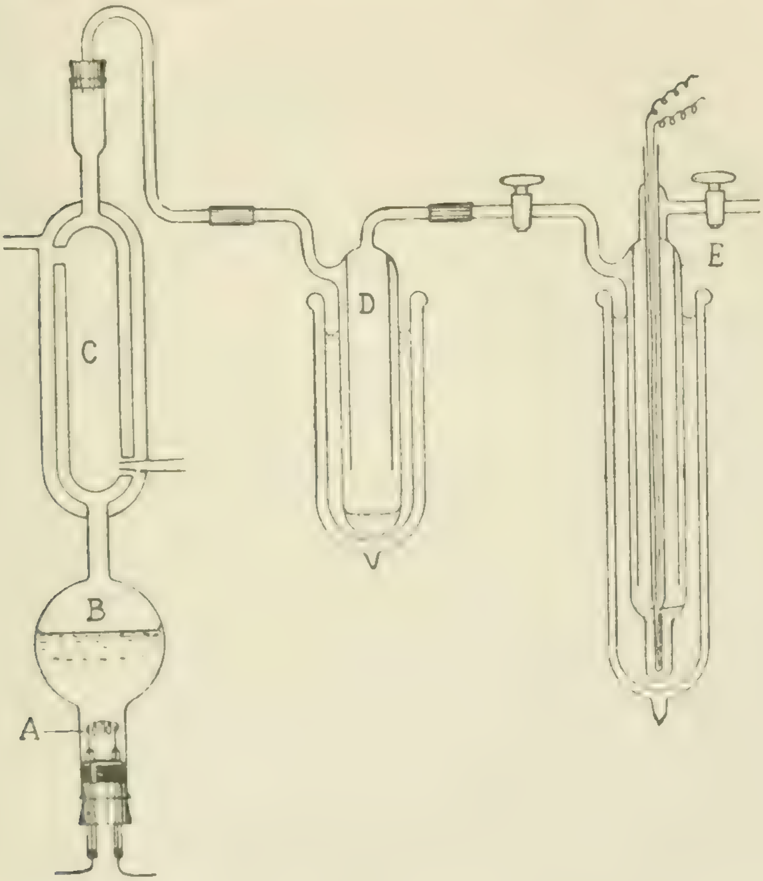
Galway.

CLXXXVIII.—*Keten.*

By Norman Thomas Mortimer Wilsmore.

Some time ago, Dr. A. W. Stewart and I attempted to prepare a series of compounds which, we thought, might have a transitory existence during the course of certain isomeric changes. To this end, the original substances were subjected to the action of a strongly heated wire, somewhat in the way described by Löb (*Zeitsch. Elektrochem.*, 1904, **10**, 504). The method was modified, however, in that the wire was kept below the surface of the liquid or solution, instead of being placed in the vapour space above it, as we believed that, by this means, any initial products of the reaction would be more easily swept away from the hot zone before they could be further decomposed. In the course of the work, we were led to try the action of the hot wire on a variety of substances. Most of the results obtained have no bearing on the present paper; but, in the case of ethyl acetate, acetone, and especially of acetic anhydride, we found that the gases given off contained a substance which had a peculiar pungent smell, and which could be condensed to a liquid in a bath of solid carbon dioxide and acetone. We gave a preliminary description of this substance in a letter to *Nature* (1907, 75, 510), and we suggested that it might be the lowest member of the keten series. Since then, Dr. Stewart has been unfortunately prevented from taking an active part in the work. In the present communication, I propose to offer further evidence in support of the above suggestion.



The apparatus used for the isolation of the new substance is shown in the accompanying figure. *A* is the heating coil of thin wire. Hitherto platinum has been used for this, but probably other difficultly fusible metals would serve as well. This wire must be renewed frequently, as it quickly becomes covered with a hard, elastic coating, which greatly reduces its activity. An arc, burning between carbon or metallic electrodes, may be substituted for the heating coil; but it requires more attention, and, so far, the results have not been so good. The heating coil is attached to leads of stout platinum wire, sealed into glass tubes, which pass through the rubber stopper as shown. A layer of mercury protects the rubber stopper from the action of the hot liquid contained in the vessel *B*. The latter is sealed directly to the double-surface reflux condenser, *C*. The trap, *D*, which is cooled by means of solid carbon dioxide and acetone, serves to catch any spray or vapour of the original liquid in *B* which may escape from *C*. The vessel, *E*, in which the substance is finally condensed, is immersed in a cooling-bath, kept at about –100° by suitable addition of liquid air. The tube in the centre of *E* is closed at the lower end, and contains a thermo-junction for measuring the temperature. To fractionate any liquid which has condensed in *E*, the latter is first cooled in a bath of liquid air. This bath is then replaced by a glass jacket, covered, except at its closed lower end, with some insulating material, and the whole is placed on a block of metal, which, by conducting heat to the bottom of *E*, produces the effect of a small, naked flame in an ordinary distillation. A few platinum "tetrahedra" facilitate ebullition.

I have not yet succeeded in obtaining the new compound in a very pure state. Carbon dioxide, acetylene, and other hydrocarbons are always liquefied along with it, and cannot be easily separated by fractional distillation; also, its tendency to condense on standing at the ordinary temperature and its great reactivity increase the difficulty of manipulation. Nevertheless, four analyses gave as a mean result that, on exploding 1 volume of the gas with excess of dry oxygen, there was a contraction of 1·09 volumes, whilst the residue contained 1·97 volumes of carbon dioxide, and 2·08 volumes of oxygen had disappeared. The corresponding numbers for a gas having the composition C_2H_2O should be 1 : 1 : 2 : 2. Also, three determinations of the density, by direct weighing in a bulb of about 150 c.c. capacity, gave 41·4 as a mean value for the molecular weight, instead of 42.

As far as they have yet been studied, the reactions of the substance correspond with those of the ketens as described by Staudinger (*Ber.*, 1905, **38**, 1735; 1906, **39**, 968, 3062; 1907, **40**, 1145; *Annalen*, 1907, **356**, 51). Thus, in general, it behaves as an internal anhydride of acetic acid. With ethyl and amyl alcohols, it gave the corresponding acetic esters, recognised by their smell, and by their giving the ferric chloride reaction for acetates after saponification. Also, in the case of the ethyl ester, a sample was obtained which, after distillation from phosphorus pentoxide, boiled at 76°. Primary amines absorb the gas rapidly at the ordinary temperature. With aniline, acetanilide was formed, which, after recrystallisation from benzene, or even after evaporating off the excess of aniline on a watch-glass in the cold, melted sharply at 112°. The melting point was not altered by fusing with pure acetanilide made in the usual way. Similarly, from *o*-toluidine, aceto-*o*-toluidide, melting at 110°, was produced, and, from anhydrous liquid ammonia, acetamide, melting at 79°. The substance reacted vigorously with bromine. On distilling off the excess of bromine and adding alcohol to the residue, there was a further evolution of heat, and the residue had the characteristic pungent smell of bromoacetic ester, indicating that bromoacetyl bromide had first been formed.

There can therefore be no doubt that the new substance is a *keten*, having the formula $CH_2:CO$, although, as distinguished from Staudinger's disubstituted ketens, it may also exist in the form $CH:C\cdot OH$.

Since all the above-mentioned reactions begin readily at the ordinary temperature, and are, in fact, accompanied by evolution of heat, keten seems likely to prove a useful acetylating agent. It has a special advantage over other acetylating agents in that no by products are formed in the reaction.

Keten has a peculiar penetrating smell, which persists for many hours if the gas has been inhaled in any but small quantities, and it attacks the mucous membranes. It is colourless in both the liquid and gaseous states, and on freezing it forms a white solid. It does not appear to react with dry oxygen, but it combines rapidly with water, forming, for the most part, acetic acid. The aqueous solution, however, also gives the chief reactions for an aldehyde, so that glycollaldehyde may be formed in small quantity at the same time. It may be noted here that, if keten could be made to react with water in the isomeric form $CH:CO\cdot H$, there would be a possibility of building up from it compounds containing the group $\cdot CH(OH)\cdot CH(OH)\cdot$.

The tendency of keten to condense on standing to a brown liquid has been already referred to. In the gaseous state, at the ordinary temperature and pressure, the reaction is fairly slow, that is to say, it is possible, by working quickly, to obtain a fair measurement of the gas in a gas burette, and the rate is further diminished by dilution with an indifferent gas. But in the liquid state, under pressure, the change is rapid and much heat is evolved. Porous substances, such as glass-wool, also hasten the reaction. The condensation product has not yet been studied.

The research is being continued.

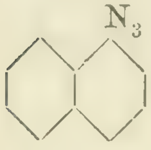
UNIVERSITY COLLEGE,
UNIVERSITY OF LONDON

CLXXXIX.—*Aromatic Azoimides. Part III. The Naphthylazoimides and their Nitro-Derivatives.*

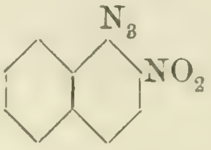
By Martin Onslow Forster and Hans Eduard Fierz.

The failure of an attempt to explain the peculiar behaviour of camphorylazoimide from a study of the hydroxyphenylazoimides (this vol., 855 and 1350) led us to consider the possibilities of other triazo-compounds, and derivatives of partly hydrogenised naphthalene suggested themselves. There is, however, no available information respecting the azoimides of naphthalene itself, and the present communication deals with this matter, as preliminary to the investigation of the compounds which might be expected to bear more directly on the original problem.

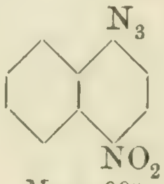
The principle interest with which previous work has invested the aromatic azoimides lies in the influence exerted on the properties of the triazo-group by neighbouring substituents. Many examples of this correlation might be quoted, such as the elimination of hydrazoic acid from *p*-nitrophenylazoimide by alcoholic potash, the removal of nitrogen from benzylazoimide by acids, and the colour change undergone by the potassium derivative of *p*-hydroxyphenylazoimide. In dealing with substituted azoimides of the naphthalene series, it was in the first place desirable to ascertain the relationship between the nitro- and triazo-groups with respect to the possibility of eliminating the latter with alcoholic potash. Noelting, Grandmougin, and Michel (*Ber.*, 1892, **25**, 3328) investigated this point in connexion with the nitrophenylazoimides, and have shown that the nitro-group is without influence in the meta-position, the change in question occurring only with ortho- and para-derivatives. We find that whilst the α- and β-naphthylazoimides resist the action of alcoholic potash, and that homonuclear nitro-groups in the favourable positions encourage elimination of hydrazoic acid, heteronuclear substitution appears to be inefficacious. The following compounds have been prepared and examined from the standpoint indicated:



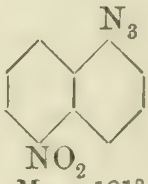
M. p. 12°.



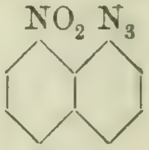
M. p. 103—104°.



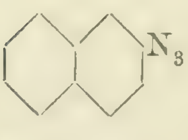
M. p. 99°.



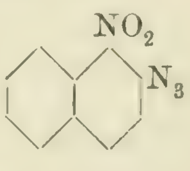
M. p. 121°.



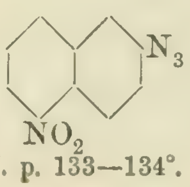
M. p. 130—131°.



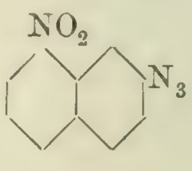
M. p. 33°.



M. p. 116—117°.

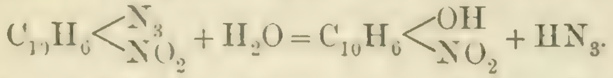


M. p. 133—134°.



M. p. 108°.

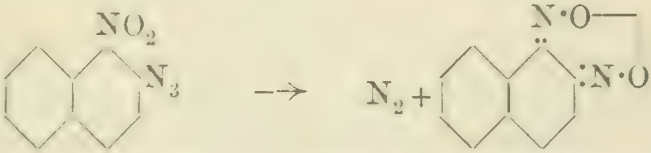
The only members of this series which yield hydrazoic acid under the influence of alcoholic potash are 2-nitro-1-naphthylazoimide, 4-nitro-1-naphthylazoimide, and 1-nitro-2-naphthylazoimide; of these, the first-named yields about 50 per cent. of the hydrazoic acid required by theory as compared with 30 per cent. obtainable from *o*-nitrophenylazoimide, whilst the para-compound, 4-nitro-1-naphthylazoimide, is resolved quantitatively into 4-nitro-1-naphthol and hydrazoic acid:



$$C_{10}H_6<\begin{matrix}N_3\\NO_2\end{matrix} + H_2O = C_{10}H_6<\begin{matrix}OH\\NO_2\end{matrix} + HN_3.$$

The smoothness of this reaction compares favourably with the corresponding change undergone by *p*-nitrophenylazoimide, which yields only 40 per cent. of the hydrazoic acid required by theory (Noelting, Grandmougin, and Michel, *loc. cit.*), whilst *p*-nitrophenol could not be recognised in the product, having undergone ethylation and reduction to *p*-azoxyphenetole.

It was to be expected that, hydrazoic acid being obtainable from 2-nitro-1-naphthylazoimide, the closely related ortho-derivative of the *β*-series, namely, 1-nitro-2-naphthylazoimide, would also part with its triazo-group. But although 30 per cent. can be obtained under favourable conditions, the reaction is complicated by a remarkable change which takes place slowly when the dissolved substance is warmed alone in alcohol, involving loss of nitrogen in two atomic proportions; in glacial acetic acid at 110°, the alteration proceeds quantitatively, and there arises the peroxide of *β*-naphthaquinonedioxime:



Noelting and his collaborators refer to the fact that *o*-nitrophenylazoimide (m. p. 51—52°) decomposes at 75—80°, yielding a volatile compound melting at 65—67° (*loc. cit.*, p. 3339), whilst Zincke (*J. pr. Chem.*, 1896, [ii], **53**, 340; compare also Drost, *Annalen*, 1899, **307**, 46), investigating several typical *o*-nitro-derivatives of phenylazoimide, has shown that all such compounds lose two nitrogen atoms, furnishing products which he describes as ortho-dinitroso-compounds. We venture to think that this view of their constitution is misleading, and take the opportunity of drawing attention to the matter, because a considerable number of such compounds have been prepared by various workers, and catalogued in the literature as dinitroso-derivatives, when really they should have been indexed as quinonedioxime peroxides. The following is a list of such derivatives:

1:2-Dinitrosonaphthalene (Koreff, *Ber.*, 1886, **19**, 182, and von Ilinski, *Ber.*, 1886, **19**, 349).

p-Dinitrosobenzene (Nietzki and Kehrmann, *Ber.*, 1887, **20**, 615).

1 : 4-Dinitrosonaphthalene (Nietzki and Guitermann, *Ber.*, 1888, **21**, 434).

2 : 5-Dinitrosotoluene (Nietzki and Guitermann, *loc. cit.*, and Mehne, *Ber.*, 1888, **21**, 734).

2 : 5-Dinitroso-*p*-xylene (Pflug, *Annalen*, 1889, **255**, 176).

o-Dinitrosobenzene (Zincke and Schwarz, *Annalen*, 1899, **307**, 36).

2 : 3- and 3 : 4-Dinitrosotoluenes (Zincke and Schwarz, *loc. cit.*).

4 : 5-Dinitroso-*m*-xylene (Zincke and Schwarz, *loc. cit.*).

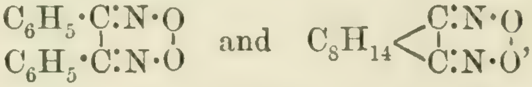
p-Dinitrosoanisole (Best, *Annalen*, 1889, **255**, 187).

p-Dinitrosocymene (Kehrmann and Messinger, *Ber.*, 1890, **23**, 3560).

Nitro-derivatives of *o*-dinitrosobenzene (Drost, *Annalen*, 1899, **307**, 46).

1 : 2 : 3 : 4-Tetranitrosobenzene (Nietzki and Geese, *Ber.*, 1899, **32**, 505).

The above compounds were prepared from the corresponding dioximes by oxidation, generally in alkaline solution with potassium ferricyanide; some of them have been shown to yield the original dioxime when carefully reduced, and in no case do the physical properties suggest the presence of a true nitroso-group. It is therefore more reasonable to regard them as analogous to the peroxides of benzildioxime and camphorquinonedioxime,



$$\begin{array}{l} C_6H_5\cdot \overset{}{C}{:}N\cdot O \\ C_6H_5\cdot C{:}N\cdot O \end{array} \quad \text{and} \quad C_8H_{14}{<}\begin{array}{l} C{:}N\cdot O \\ C{:}N\cdot O \end{array},$$

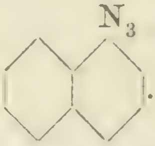
neither of which can possibly be classified as normal nitroso-compounds. None of the authors who describe the compounds enumerated appears to attach much importance to the alternative constitution, excepting Koreff (*Ber.*, 1886, **19**, 183); some among the other authors content themselves with mentioning the peroxide formula, while retaining the misleading name, and the remaining ones ignore it altogether. Moreover, Auwers and Meyer (*Ber.*, 1888, **21**, 804) and Scholl (*Ber.*, 1890, **23**, 3497) refer to the work of Koreff, without pointing out the unlikelihood of the derivatives described by him being genuine nitroso-compounds, whilst Bridge (*Annalen*, 1893, **277**, 79) states that the oxidation product obtained by Nietzki and Kehrmann (*Ber.*, 1887, **20**, 615) from quinonedioxime must be regarded as *p*-dinitrosobenzene. As recently as 1903, the peroxides of *o*-benzoquinonedioxime and of diquinoyltetroxime are referred to erroneously as *o*-dinitrosobenzene and tetranitrosobenzene respectively (Julius Schmidt, "Die Nitrosoverbindungen"; Ahrens' *Vorträge*, Vol. VIII).

On comparing the behaviour of 2-nitro-1-naphthylazoimide with that of 1-nitro-2-naphthylazoimide, it is found that the former substance loses nitrogen much less readily, solutions in glacial acetic acid and in xylene appearing to undergo no change when boiled; the solid material, however, begins to yield gas above the point of fusion, decomposition proceeding rapidly at about 150°. From this it is evident that the *a*-position for the triazo-group is less favourable to the change in question than the neighbouring one, and examination of the other nitronaphthylazoimides indicates that only those in which the nitro-group has assumed the ortho-position give rise to a definite product of decomposition. The facility with which the change occurred in the case of 1-nitro-2-naphthylazoimide encouraged us to hope that it might be possible to obtain, through its dioxime peroxide, the hitherto unknown 1:5-naphthaquinone, because these positions are sympathetic, and the recent work of Willstätter has established the existence of an amphi-naphthaquinone, namely, the 2:6-derivative (Willstätter and Parnas, *Ber.*, 1907, **40**, 1406). The attempt failed, however, and we were unsuccessful also in the case of the 1:8-derivative, but it is well known that a structural difficulty presents an obstacle to formulating the peri-naphthaquinone.

In this communication, we describe the azoimides from seven nitronaphthylamines. They are coloured various shades of brown and yellow, but darken rapidly when exposed to light; the substances crystallise with such readiness, and are prepared so easily from the respective naphthylamines, that they offer a means of identifying small quantities of these bases.

Experimental.

a-Naphthylazoimide,



In the first attempts to prepare this compound, we made use of the method which gave satisfactory results in the case of *p*-hydroxyphenylazoimide, namely, the action of hydroxylamine on the diazonium salt (E. Fischer, *Annalen*, 1877, **190**, 96); the discouraging yield, which amounted to less than 5 per cent., led us to try the action of hydrazine, but in this case also the proportion of azoimide obtained was trifling, the greater part of the material remaining after steam distillation in the form of a tough, black resin, which develops a beautiful greenish-blue coloration with concentrated sulphuric acid. No variation in the experimental conditions leading to improvement, we had recourse ultimately to the method described by Noelting and Michel (*Ber.*, 1893, **26**, 86), which consists in treating the diazonium salt with hydrazoic acid.

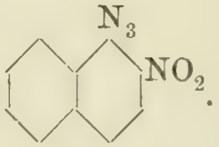
Thirty grams of *a*-naphthylamine dissolved in 180 c.c. of glacial acetic acid were mixed with 80 c.c. of concentrated sulphuric acid and diazotised with a solution of sodium nitrite containing 15 grams; after ten minutes, 5 grams of powdered carbamide were added to the ice-cold liquid, followed by 15 grams of sodium azide in 50 c.c. of water. A colourless turbidity was immediately developed, and torrents of nitrogen escaped. After several hours at zero, the oil was extracted with ether, the residue from which was then distilled in a current of steam, four hours being required to complete this process. The ethereal solution of the distillate was pale brown, but lost the colour in two extractions with concentrated hydrochloric acid followed by 20 per cent. potash, and, when dried with calcium chloride, left on evaporation 27 grams of pale yellow, limpid oil, which crystallised in hard, lustrous prisms melting at 12°:

0·1993 gave 43·4 c.c. of nitrogen at 21° and 742 mm. N = 24·77.

$C_{10}H_7N_3$ requires N = 24·85 per cent.

The substance has the persistent odour of ethoxynaphthalene; it is readily soluble in alcohol, and mixes in all proportions with ether or acetone. An attempt to distil under 2 mm. pressure was unsuccessful, decomposition taking place at about 110°. Like all the azoimides described in this paper, it is decomposed with great vigour by concentrated sulphuric acid, torrents of nitrogen being evolved. Alcoholic potash failed to eliminate hydrazoic acid from α-naphthylazoimide, which was recovered unaltered after three days' treatment with the boiling agent. Nitration proceeded with unusual smoothness, 5 grams of the oil when mixed with 30 c.c. of nitric acid (sp. gr. 1·42) becoming solid in less than two minutes; the sole product was 4-nitro-1-naphthylazoimide (see below).

2-*Nitro*-1-*naphthylazoimide*,



The 2-nitro-1-naphthylamine required for preparing this azoimide was made by the process of Lellmann and Remy (*Ber.*, 1886, **19**, 802 and 893). Instead of nitrating the α-acetonaphthalide with nitric acid of sp. gr. 1·51, however, we used the corresponding quantity of the weaker agent, sp. gr. 1·42, and checked the tendency to subsidiary changes by adding carbamide. This is advantageous when the 4:1-nitro-base is required, because the temperature may be then raised to 30° or 35°, when it is found that 100 grams of α-acetonaphthalide yield only 30 grams of the molecular mixture of 4:1- and 2:1-nitro-compounds, instead of the 60 grams obtained at 15°, the remainder in each case consisting of 4-nitro-1-acetonaphthalide, which remains dissolved in the glacial acetic acid. The 2-nitro-1-acetonaphthalide was hydrolysed with boiling dilute sulphuric acid and alcohol, which furnishes a quantitative yield of the nitro-base in two days; it is therefore more convenient than alcoholic potash, which hydrolyses a portion of the nitro-compound to 2-nitro-1-naphthol.

The 2-nitro-1-naphthylamine was diazotised in a mixture of glacial acetic acid and concentrated sulphuric acid, and, in presence of carbamide, treated with hydrazoic acid; this led to immediate precipitation of the azoimide, which, when crystallised from dilute acetone, formed long, lustrous, yellow needles, melting at 103—104°, and decomposing very slowly at that temperature:

0·1073 gave 24·6 c.c. of nitrogen at 21° and 760 mm. N = 26·22.

$C_{10}H_6O_2N_4$ requires N = 26·16 per cent.

The compound is readily soluble in acetone, alcohol, or benzene, but hot petroleum dissolves it only sparingly.

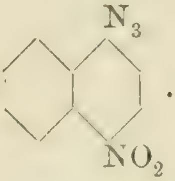
Decomposition by Heat.—The behaviour of the 2-nitro-1-naphthylazoimide when heated is quite distinct from that of the isomeric 1-nitro-2-naphthylazoimide, although the product of the change is the same in each case. Solutions in glacial acetic acid, xylene, and aniline were boiled without yielding nitrogen, and the compound was recovered unchanged, although somewhat contaminated, from the last-named solvent. When heated alone, 2-nitro-1-naphthylazoimide begins to liberate gas very slowly above the melting point, effervescence becoming brisk towards 150°; the product was found to be identical with the β-naphthaquinonedioxime peroxide obtained from the isomeric 1-nitro-2-naphthylazomide, crystallising from dilute alcohol in almost colourless needles melting at 127° without decomposition (von Ilinski, *Ber.*, 1886, **19**, 349; see also Koreff, *loc. cit.*, p. 176):

0·2631 gave 34·4 c.c. of nitrogen at 22° and 756 mm. N = 15·15.

$C_{10}H_6O_2N_2$ requires N = 15·06 per cent.

Hydrolysis.—Four grams of the azoimide were heated in alcohol with 40 c.c. of 5 per cent. potash during eight hours under reflux, red crystals of the potassium derivative of 2-nitro-1-naphthol appearing early in the experiment; cold dilute sulphuric acid was added to the residue left by evaporation, and on distilling the filtrate, and neutralising the distillate, 0·6 gram of sodium azide was obtained, corresponding roughly to 50 per cent. of that required by theory. The nitronaphthol was recrystallised from alcohol, and melted at 128°.

4-*Nitro*-1-*naphthylazoimide*,

 .

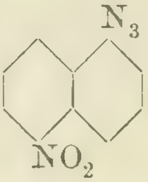
The azoimide separated immediately on adding sodium azide to a solution of the diazonium salt from 4-nitro-1-naphthylamine; when recrystallised from boiling alcohol, it formed long, lustrous, yellow needles melting sharply at 99°:

0·0930 gave 21·5 c.c. of nitrogen at 20° and 757 mm. N = 26·45.
$C_{10}H_6O_2N_4$ requires N = 26·16 per cent.

The compound is identical with the product of nitrating 1-naphthylazoimide; it dissolves very sparingly in cold methyl and ethyl alcohols, in benzene, and in hot petroleum. All attempts to convert the substance into α-naphthaquinonedioxime peroxide by eliminating nitrogen were unsuccessful.

Hydrolysis.—Hot alcoholic potash resolved 5 grams into 2·5 grams of 4-nitro-1-naphthol (m. p. 164·5°) and 1·2 grams of sodium azide; the yield of the latter was therefore quantitative.

5-*Nitro*-1-*naphthylazoimide*,

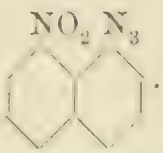
 .

5-Nitro-1-naphthylamine, prepared by reducing 1:5-dinitronaphthylamine with alcoholic ammonium sulphide and recrystallising the product from water, was diazotised and treated with hydrazoic acid; the azoimide appeared forthwith as a greenish-yellow precipitate, and was recrystallised from boiling absolute alcohol, which deposits the substance in lustrous, yellow needles melting at 121°:

0·1949 gave 44·6 c.c. of nitrogen at 23° and 764 mm. N = 26·53.
$C_{10}H_6O_2N_4$ requires 26·16 per cent.

Decomposition takes place rapidly at 130°, but the product is a tar, in which it has not been possible to recognise the peroxide of 1:5-naphthaquinonedioxime. An attempt to hydrolyse the azoimide with alcoholic potash converted the substance into a black powder, which could not be identified; no trace of hydrazoic acid was recognisable, however.

8-*Nitro-1-naphthylazoimide*,



The peri-nitronaphthylamine required for this preparation was made according to the directions of Meldola and Streatfeild (Trans., 1893, **63**, 1055), based on those of Noelting and Collin (*Ber.*, 1884, **17**, 261). In the hope of improving the yield obtained by these chemists (6—8 per cent.), twelve experiments, each involving 200 grams of α-naphthylamine, were carried out under conditions varying in respect of time, temperature, and strength of acid from those laid down; we were unsuccessful, however, and found, furthermore, that the presence of carbamide during nitration does not appear to influence the result to any marked extent. On one occasion, 20 grams was obtained, but it was not possible to recognise the particular modification in the conditions which led to this result, and we could not repeat it. Instead of dissolving the crude base in dilute sulphuric acid for the purpose of purification, it was found more convenient to dissolve the dry product in a small quantity of benzene and precipitate the tar with petroleum (b. p. 80—100°), the decanted liquid being then treated with further quantities of petroleum until crystals alone separate.

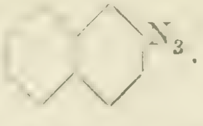
The conversion of peri-nitronaphthylamine into 8-nitro-1-naphthylazoimide proceeded in the normal fashion, and the product was recrystallised twice from hot acetone, which deposits hard, lustrous, colourless prisms, melting at 130—131° with decomposition; the substance is extremely sensitive to light, the crystals becoming pink during a few minutes' exposure:

0·1250 gave 29·0 c.c. of nitrogen at 22° and 747 mm. N = 26·39.

$C_{10}H_6O_2N_4$ requires N = 26·16 per cent.

Having in view the possibility of obtaining the peroxide of peri-naphthaquinonedioxime, the azoimide was heated in boiling glacial acetic acid, in xylene, and in aniline, but in no case did the required change take place. Moreover, continued boiling with alcoholic potash failed to eliminate hydrazoic acid, the azoimide being rapidly converted into unrecognisable products of complete decomposition.

β-*Naphthylazoimide*,

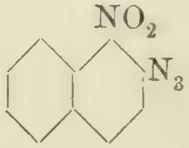


As in the case of α-naphthylamine, we compared the commoner methods of converting the base into the azoimide, finding as before that no process is comparable for convenience and cleanliness with that of Noelting and Michel. The application of the hydroxylamine method to β-naphthylamine, however, was more successful than in the case of the isomeric substance, and a yield of 50 per cent. was obtained instead of only 5 per cent.; the remainder would appear to be converted into 2:2-azoxynaphthalene, obtained by Meisenheimer and Witte by reducing 2-nitronaphthalene with sodium stannite (*Ber.*, 1903, **36**, 4163). The hydrazine method gave about 20 per cent., but the product was not a good specimen, and ultimately the azoimide was prepared by adding sodium azide to diazotised β-naphthylamine in presence of carbamide, the quantities employed being the same as those already mentioned for α-naphthylazoimide. After steam distillation, which proceeds very slowly, the dried product was mixed with a small quantity of petroleum and cooled in ice, when the azoimide crystallised in lustrous needles melting at 33°:

0·2486 gave 53·4 c.c. of nitrogen at 21° and 761 mm. N = 24·97

$C_{10}H_7N_3$ requires N = 24·85 per cent.

β-Naphthylazoimide has the odour of ethoxynaphthalene; it is less sensitive to light than the nitro-derivatives, becoming yellow on continued exposure. The substance is freely soluble in organic media, dissolving less readily in methyl and ethyl alcohols, from which, however, it cannot be crystallised, as it separates as an oil on dilution; boiling water dissolves it very sparingly, and dilute solutions deposit lustrous, colourless leaflets resembling β-naphthylamine. Moderately concentrated sulphuric acid (66 per cent.) liberates two-thirds of the azidic nitrogen (16·18 per cent. instead of the calculated 16·52 per cent.), but it has not been possible to recognise the corresponding aminonaphthol in the product. Alcoholic potash does not eliminate hydrazoic acid.

1-*Nitro-2-naphthylazoimide*, 

This compound has been obtained by direct nitration of β-naphthylazoimide with acid of sp. gr. 1·42, and also by the action of hydrazoic acid on diazotised 1-nitro-2-naphthylamine; it was recrystallised twice from acetone, which deposited pale yellow, silky needles melting at 116—117° with vigorous gas evolution:

0·1556 gave 35·8 c.c. of nitrogen at 24° and 756 mm. N = 26·27.

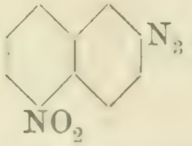
$C_{10}H_6O_2N_4$ requires N = 26·16 per cent.

When reduced with alcoholic ammonium sulphide, a quantitative yield of 1-nitro-2-naphthylamine was obtained, m. p. 126—127°. Eighty per cent. sulphuric acid liberated two-thirds of the azidic nitrogen (12·47 per cent. instead of the calculated 13·08 per cent.).

Decomposition by Heat.—The readiness with which the substance loses nitrogen precludes the use of alcohol or solvents of higher boiling point for recrystallisation ; a solution in glacial acetic acid undergoes no change at 50°, but as the temperature rises above this point, gas is evolved in quickly augmenting proportions, the effervescence being quite vigorous at 110°. When this change is complete, dilution with water precipitates the peroxide of *β*-naphthaquinonedioxime, which is thus produced much more readily from the 1-nitro-2-azoimide than from the isomeric 2-nitro-1-azoimide.

Hydrolysis.—Twelve grams were heated with 100 c.c. of 4 per cent. methyl-alcoholic potash in a reflux apparatus during eight hours ; on cooling the dark red liquid, lustrous needles of the dioxime peroxide separated. The residue from the evaporated liquid was taken up with water, filtered from a further quantity of the dioxime peroxide, mixed with a small proportion of a substance which was not identified, acidified, and distilled in steam, when hydrazoic acid corresponding to about 30 per cent. of the amount required by theory was obtained.

5-*Nitro*-2-*naphthylazoimide*,



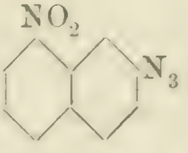
The 5-nitro-2-naphthylamine employed in this preparation was obtained in association with a smaller proportion of 8-nitro-2-naphthylamine by the process of Friedländer and Szymanski (*Ber.*, 1892, **25**, 2077), which consists in adding *β*-naphthylamine nitrate to concentrated sulphuric acid at −10°. The azoimide prepared from the first-named base was obtained from acetone in lustrous, brownish-yellow needles melting at 133·5°.

0·1923 gave 43·8 c.c. of nitrogen at 18° and 744 mm. N = 26·16.

$C_{10}H_6O_2N_4$ requires N = 26·16 per cent.

The substance is readily soluble in hot methyl and ethyl alcohols, dissolving very freely in ethyl acetate and in glacial acetic acid. There is no sign of gas evolution when the solutions are heated, and hot alcoholic potash has failed to eliminate hydrazoic acid.

8-*Nitro*-2-*naphthylazoimide*,



The production of this derivative from 8-nitro-2-naphthylamine proceeded smoothly, the conversion of the diazonium salt into nitro-azoimide, as in the case of all described in this paper, being quantitative. Crystallisation from dilute acetone gave lustrous, yellow prisms melting at 108°:

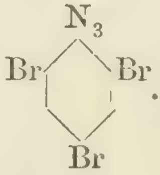
0·1324 gave 30·8 c.c. of nitrogen at 23° and 744 mm. N = 26·26
$C_{10}H_6O_2N_2$ requires N = 26·16 per cent.

It was not possible to detect hydrazoic acid as a product of heating 8-nitro-2-naphthylazoimide with alcoholic potash, and there was no tendency to pass into a dioxime peroxide on heating the material alone.

Preparation of Substituted Azoimides According to Noelting and Michel.

In working through the series just described, it has appeared to us that the regularity of the method first described by Noelting and Michel (*Ber.*, 1893, **26**, 86) is very significant. The general analogy which has been recognised as connecting the triazo-group with the halogens receives further confirmation from this reaction, which would seem to be applicable to any base capable of undergoing conversion into a diazonium salt, always provided that free mineral acid has no action on the resulting azoimide, a clause which precludes its use in the case of ortho- and para-hydroxyphenylazoimides (this vol., 855 and 1350). In dealing with complex bases likely to suffer undesirable alteration when the diazonium salts are treated with bromine followed by ammonia, the method is invaluable.

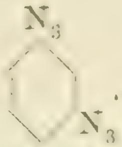
Two examples of its application to delicate cases may be added to those already described.

s-Tribromophenylazoimide, .—Silberstein (*J. pr. Chem.*, 1883, [ii], **27**, 113) claims to have prepared this compound by heating tribromobenzenediazonium nitrate dissolved in concentrated hydrochloric acid until crystals separate—these crystals being regarded as "tribromobenzenediazonium chloride perbromide"—and treating the product with ammonia; no bromine was added, and it is to be presumed that this halogen was regarded as arising by decomposing a portion of the tribromobenzenediazonium salt. He describes tribromophenylazoimide produced in this way as forming colourless needles melting at 59°. We think, however, that Silberstein had another substance in hand, because the product obtained from diazotised tribromoaniline and hydrazoic acid crystallises from alcohol in long, lustrous, colourless needles, melting at 72°, and quickly becoming pink when exposed to light:

0·1816 gave 18·7 c.c. of nitrogen at 24° and 772 mm. N = 12·03.
0·3570 ,, 0·5621 AgBr. Br = 67·00.

$C_6H_2Br_3N_3$ requires N = 11·83 ; Br = 67·38 per cent.

Contrary to the statement of Silberstein, the substance is not volatile in steam.

m-*Bistriazobenzene*,  .—Six grams of *m*-phenylenediamine hydrochloride were dissolved in 50 c.c. of 50 per cent. sulphuric acid, and treated with 4 grams of sodium azide ; 6 grams of sodium nitrite were then added to the ice-cold liquid, followed by a further 4 grams of sodium azide. After one hour, the emulsion was extracted with ether, and the residue left by this on evaporation was distilled twice in steam. The bistriazobenzene forms long, lustrous, faintly yellow needles, melting at 5° ; when heated quickly on a spatula, it does not explode, but concentrated sulphuric acid gives a brilliant flame, accompanied by a slight detonation.

From the recorded description of *p*-bistriazobenzene (Griess, *Ber.*, 1888, **21**, 1561 ; Silberrad, Trans., 1906, **89**, 171), it is evident that the meta-compound is much less dangerous ; a direct determination of nitrogen was made without mishap by mixing the substance in a weighed tube with potassium dichromate and copper oxide, the tube being then enclosed in a roll of oxidised copper gauze :

0·1276 gave 59·6 c.c. of nitrogen at 23° and 743 mm. N = 52·73.

$C_6H_4N_6$ requires N = 52·50 per cent.

In the foregoing experiment there was no detonation, but one attempt to estimate carbon and hydrogen was spoiled by a slight explosion, which dispersed the vapour too rapidly in the tube without shattering the apparatus ; another combustion by the ordinary process was completed, but the carbon percentage was indicated at about 2 per cent. in excess of that required by theory, which is hardly surprising. Decomposition with 80 per cent. sulphuric acid gave results in agreement with the usual behaviour of azoimides towards this agent :

0·1868 gave 56·4 c.c. of nitrogen at 22° and 767 mm. N = 35·26.

$C_6H_4N_6$ requires 2/3 N = 35·04 per cent.

m-Bistriazobenzene has a faint, but characteristic, odour of decayed apples ; the inhaled vapour gives rise to a throbbing sensation at the base of the forehead.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CXC.—*The Action of Phosphorus Pentachloride on Hydroxytrimethylsuccinic Ester.* 1 : 2-*Dimethylcyclopropane*-1 : 2-*dicarboxylic Acid* (1 : 2-*Dimethyltrimethylene*-1 : 2-*dicarboxylic Acid*).

By Herbert Henstock and Bertha Elizabeth Woolley.

The experiments described in this paper were undertaken at the request of Professor W. A. Bone, in order to clear up an outstanding point of some interest, connected with the investigations on the substituted succinic acids carried out by himself in conjunction with Mr. Sprankling and other collaborators (Trans., 1899, **75**, 839; 1900, **77**, 654, 1298; 1902, **81**, 50).

In one of their papers (Trans., 1902, **81**, 50), Bone and Sprankling described a methylenedimethylsuccinic acid, $C_7H_{10}O_4$ (m. p. 141°), obtained by the action of diethylaniline on bromotrimethylsuccinic anhydride. The properties of this acid were subsequently further examined by Bone and Henstock (Trans., 1903, **83**, 1380), and the conclusion as to its unsaturated character was confirmed by the determination of the magnetic rotation of its diethyl ester by the late Sir William Perkin (*ibid.*, 1903, **83**, 1389).

In the year 1900, however, Paolini (*Gazzetta*, 1900, **30**, (ii), 497), following up the work of Komppa (*Act. Soc. Sc. Fennicae*, 1898, **24**, 1; Abstr., 1899, i, 419), had described an isomeric acid, $C_7H_{10}O_4$, melting at 153°, obtained by a process (see below) which probably involved the elimination of hydrogen chloride from chlorotrimethylsuccinic ester. The fact that his acid neither decolorised cold alkaline permanganate nor exhibited any tendency to form an additive compound with hydrogen bromide at the ordinary temperature, led Paolini to regard it as a saturated compound, and he described it as 1 : 2-dimethyltrimethylene-1 : 2-dicarboxylic acid (1 : 2-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid). It seemed important to repeat Paolini's work and to examine the properties of his acid, for in the event of its cyclic character being confirmed, there would appear to be a remarkable difference in the behaviour of bromotrimethylsuccinic anhydride and chlorotrimethylsuccinic ester, under conditions involving the elimination of the hydrogen halide. The starting point for the preparation of Paolini's acid is dimethylacetoacetic ester, which on treatment with hydrogen cyanide, according to the method detailed by Komppa, and subsequent hydrolysis of the resulting cyano-ester, yields hydroxytrimethylsuccinic acid melting at 156—157°. The diethyl salt of this acid is then subjected to the action of phosphorus pentachloride in chloroform solution. On pouring the liquid into cold water and then extracting with ether, an oil is obtained, which on hydrolysis with alcoholic potash finally yields the acid under discussion. It should here be stated that Komppa, who was the first to investigate the action of phosphorus pentachloride on diethyl hydroxytrimethylsuccinate, succeeded in isolating the corresponding chloro-derivative,

$$CO_2Et\cdot CMe_2\cdot CMeCl\cdot CO_2Et,$$

which we therefore must assume to be formed in the course of the above reactions. Komppa treated this chloro derivative with alcoholic potash and obtained a crystalline compound free from chlorine, which, without further examination, he assumed to be a β-lactonecarboxylic acid.

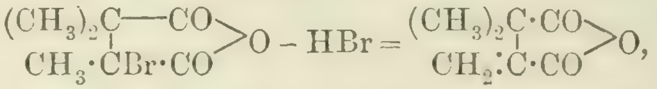
We have prepared Paolini's acid in considerable quantities and made a thorough examination of its properties, the determination of the magnetic rotation of its diethyl ester having been undertaken by the late Sir William Perkin in March last. Although the investigation was not completed, we are able to state that the magnetic rotation values of the diethyl ester left no doubt in his mind as to its saturated character, and the contrast between its optical properties (magnetic rotation and refractive power) and those of the corresponding isomeric unsaturated ester obtained by Bone and Sprankling from bromotrimethylsuccinic anhydride were, in his opinion, quite consistent with the saturated cyclic constitution which Paolini had assigned to his acid. The properties of the two isomeric acids and their diethyl esters may be tabulated as follows :

	A. Methylenedimethylsuccinic acid (Bone and Sprankling).		*B.* 1 : 2-Dimethyl*cyclo*propane-1 : 2-dicarboxylic acid (Paolini).	
Melting point	142·5°		149—150·5° (Paolini gives 153°)	
Dissociation constant at 25°	0·01670		0·0099	
Solubility in water	Very soluble (cannot be recrystallised)		Less soluble than *A* (can be readily recrystallised)	
Density 10°/10°	1·0169		1·0685	
Magnetic rotation :				
(1) Specific rotation..	1·0147	$t = 16·6°$	0·9138	$t = 18·9$
(2) Molecular ,, ..	11·925		10·5530	
Refractive power :				
Hα........................	92·360	$t = 17·4°$	88·245	$t = 13·7°$
Hβ........................	94·391		89·732	
Hγ........................	95·241		90·620	
Dispersion Hγ – Hα ...	2·881		2·375	

The structural difference between the two isomeric diethyl esters under consideration is clearly brought out by a comparison of their molecular rotations with the corresponding estimated value for diethyl trimethylsuccinate, $C_{11}H_{20}O_4$, namely, 11·205; the calculated value for the corresponding cyclic ester should be 0·6° lower, or 10·605 (Trans., 1902, **81**, 294). This is very near to the value found for Paolini's ester (10·550). On the other hand, the calculated value for the corresponding unsaturated ester will, of course, be higher than that of diethyl trimethylsuccinate by 0·7° to 1·1°; the value found for Bone and Sprankling's ester (11·925), it will be seen, was 0·72° higher. The observed difference between the molecular refractive power of the two esters is also in harmony with the supposed difference in structure, thus:

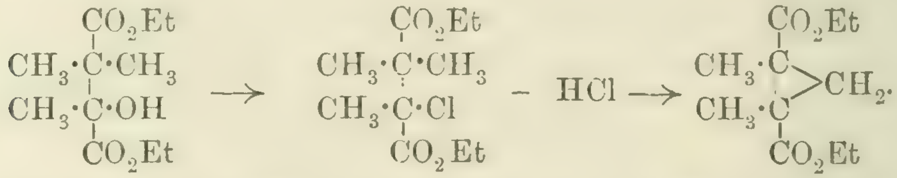
		Hα.	
		Calculated.	Found.
$C_{11}H_{18}O_4$	Saturated	90·80	88·24
	Unsaturated.........	93·18	92·26
	Difference......	2·38	4·02

It must be admitted therefore that whereas in the case of bromotrimethylsuccinic anhydride the elimination of hydrogen bromide, by the action of diethylaniline, gives rise to an unsaturated molecule:



$$\begin{array}{l}(CH_3)_2C—CO\\ CH_3\cdot CBr\cdot CO\end{array}\!\!>O - HBr = \begin{array}{l}(CH_3)_2C\cdot CO\\ CH_2\!:\!C\cdot CO\end{array}\!\!>O,$$

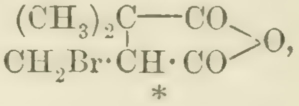
in Paolini's experiments hydrogen chloride was eliminated from chlorotrimethylsuccinic ester in such a manner as to yield a saturated compound, thus:



$$\begin{array}{c}CO_2Et\\ CH_3\cdot C\cdot CH_3\\ CH_3\cdot C\cdot OH\\ CO_2Et\end{array} \longrightarrow \begin{array}{c}CO_2Et\\ CH_3\cdot C\cdot CH_3\\ CH_3\cdot C\cdot Cl\\ CO_2Et\end{array} - HCl \longrightarrow \begin{array}{c}CO_2Et\\ CH_3\cdot C\\ CH_3\cdot C\\ CO_2Et\end{array}\!\!>CH_2.$$

The reason for this difference in behaviour is not very apparent.

Experiments which are being carried out in these laboratories seem to indicate that the bromo-anhydride may have the constitution:



$$\begin{array}{l}(CH_3)_2C—CO\\ CH_2Br\cdot \overset{}{\underset{*}{C}}H\cdot CO\end{array}\!\!>O,$$

in which case the hydrogen atom marked with an asterisk would be most likely to unite with the bromine atom when hydrogen bromide is eliminated, ring formation being thus precluded.

EXPERIMENTAL.

1 : 2-*Dimethylcyclopropane*-1 : 2-*dicarboxylic Acid.*

The preparation of hydroxytrimethylsuccinic ester and of 1 : 2-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid was carried out according to the directions of Komppa (*Ber.*, 1896, **29**, 1620) and Paolini (*loc. cit.*), and the yields compared very favourably with those obtained by these chemists.

A quantity of the diethyl ester of the acid was prepared in the usual manner and its purity determined by analysis:

0·1378 gave 0·3096 CO_2 and 0·1032 H_2O. C = 61·63; H = 8·40.
$C_{11}H_{18}O_4$ requires C = 61·68; H = 8·40 per cent.

The density and optical properties of this ester as determined by the late Sir William Perkin were as follows:

Density:

d 10°/10° = 1·0685. *d* 15°/15° = 1·0642. *d* 20°/20° = 1·0602.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
18·9°.	0·9438.	10·553.

Refractive power:

d 13·7°/4° = 1·06363.

	Index of refraction, μ.	Sp. refraction, μ − 1/*d*.	Mol. refraction, μ − 1/*d p*.
H	1·43860	0·41236	88·245
H	1·44600	0·41931	89·732
H	1·45041	0·42346	90·620

Dispersion: Hγ − Hα = 2·375.

The bearing of the above values for the magnetic rotation and refractive power on the question of the constitution of the ester and its isomerism with methylenedimethylsuccinic acid, obtained by Bone and Sprankling, has been discussed in the introductory portion of the paper (p. 1955).

1 : 2-Dimethyl*cyclo*propane-1 : 2-dicarboxylic acid, after being recrystallised from chloroform, melted at 149—150·5° (Paolini gives 153°):

0·1150 gave 0·2240 CO_2 and 0·0675 H_2O. C = 53·03; H = 6·52.
$C_7H_{10}O_4$ requires C = 53·1; H = 6·32 per cent.

0·5802 of the silver salt gave 0·3371 Ag. Ag = 58·12.
$C_7H_8O_4Ag_2$ requires Ag = 58·06 per cent.

Its ordinary physical and chemical properties agreed in nearly all instances with those described by Paolini.

The acid is very easily soluble in ether or alcohol, moderately so in water, benzene, or chloroform, and insoluble in light petroleum. It yields an insoluble calcium salt, and also a liquid anhydride. It slowly decolorises a dilute solution of alkaline permanganate in the cold. The reason of this is that possibly the alkali breaks the ring, which is considerably weakened by the presence of the two CH_3 groups; evidence of this may be seen in the fact that the unsaturated methylenedimethylsuccinic acid decolorised alkaline permanganate instantaneously, whereas an equal weight of the *cyclo*propane acid requires a minute or two to produce the same effect.

The electrical conductivity at 25° was determined with the following results:

$$\mu_\infty = 360.$$

v.	μ_v.	m.	$K=100k$.
26·42	17·86	0·0496	0·009809
52·84	24·83	0·0690	0·009680
105·68	35·09	0·0978	0·010140
211·36	48·64	0·1351	0·009985

$$K=0·009903.$$

Mixtures of this acid (α) with varying proportions of methylenedimethylsuccinic acid (β), prepared by Bone and Sprankling, melted as follows:

α.	β.	M. p.
90 per cent.	10 per cent.	126°
10 ,,	90 ,,	136
50 ,,	50 ,,	128

The authors desire to express their best thanks to Professor Bone for his kind interest and help in the matter, and also to the Research Fund Committee of the Chemical Society for a grant which enabled them to purchase the more expensive chemicals used in the work.

They were also especially indebted to the late Sir William Perkin for his great kindness in undertaking the determination of the optical properties of the ester, which so decisively proved its constitution.

THE UNIVERSITY,
MANCHESTER.

CXCI.—*The Vapour Pressures of Triethylamine, of 2 : 4 : 6-Trimethylpyridine, and of their Mixtures with Water.*

By Robert Tabor Lattey.

I. *Triethylamine and Water.*

This work was undertaken in order to obtain experimental verification of the forms predicted by theory for the total and partial vapour-pressure curves of two liquids, the miscibility of which depends on temperature. It was also hoped that a study of the properties of two liquids which are completely miscible at some temperatures and only slightly soluble one in the other at other temperatures might throw some light on the problem of the miscibility of fluids.

The forms of the vapour-pressure curves have been discussed by Duhem, Margules, Ostwald, Zawidzki, and others (for references, see Marshall, Trans., 1906, 89, 1351 *et seq.*). The experiments were begun before the appearance of Marshall's paper (*loc. cit.*), and the discussion of some theoretical points, which was intended, has been consequently rendered unnecessary.

The following symbols are used throughout this paper :

x = the ratio of the number of molecules of amine to the number of molecules of both kinds.

p_a = the partial pressure of the amine vapour.

p_w = the partial pressure of water vapour.

π = the total vapour pressure of the mixture.

Then, as has been shown by many previous authors :

$$\frac{p_a}{p_w} = -\frac{x}{1-x}\frac{dp_a}{dp_w} \quad \text{. . . . . (i)}$$

$$p_a + p_w = \pi \quad \text{. . . . . (ii)}$$

$$\frac{dp_a}{dx} + \frac{dp_w}{dx} = \frac{d\pi}{dx} \quad \text{. . . . . (iii)}$$

and consequently,

$$\frac{d\pi}{dx}(1-x) = \frac{dp_a}{dx}\left(1 - x\frac{\pi}{p_a}\right) \quad \text{. . . . . (iv).}$$

A form of this equation (iv) is used by Marshall to deduce the possible forms of partial and total vapour-pressure curves. Both he and Bose (*Physikal. Zeitsch.*, 1907, 8, 347) suggest the use of equation (i) for obtaining the values of the partial pressures when only the total pressures are known. The methods of both these authors consist in drawing probable curves, taking averages of the values of

$\frac{p_a}{p_w}$ and $-\frac{x}{1-x}\frac{dp_a}{dp_w}$ obtained from these curves, and drawing new more approximate curves. A far simpler method is to use equation (iv). From the total pressure curve, the values for π and $\frac{d\pi}{dx}$ for values of x differing by 0·05 between $x=0$ and $x=1·00$ can be tabulated. At the maximum, $x=\frac{p_a}{\pi}$, and consequently the value of p_a is known. In the neighbourhood of $x=0$ and of $x=1$, the values of $\frac{dp_a}{dx}$ and $\frac{dp_w}{dx}$ are expressed graphically by straight lines joining the points (0,0) to $(1,p_a)$ and (1,0) to $(0,p_w)$ respectively.

An approximate curve for p_a can then be drawn and the values in the neighbourhood of known points be used to calculate $\frac{dp_a}{dx}$, and consequently to correct the curvature in these neighbourhoods. It is surprising how easy the continuation of a curve once begun by this method becomes with a little practice. In portions of the curve where $\frac{d^2p}{dx^2}$ is small, $\frac{dp}{dx}$ can be taken as equal to $10(p_1-p_3)$, where p_1 and p_3 are the values of p_a or of π for $x+0·05$ and for $x-0·05$ respectively. Since the curve representing the variations of π with changes in the value of x is drawn from experimental results, its curvature will probably not be exactly determined at all points; the exact position of the maximum point, for instance, will probably not be known to within 1 or 2 per cent. If this is so, the values obtained for p_a and p_w when $x=0$ and when $x=1$ will not be correct. Multiply each set of calculated partial pressures in the ratio required to obtain a correct end-point and draw the total vapour-pressure curve so obtained alongside the original one. By this means, the position of errors in the original curve can be located and the necessary corrections made. This operation can be repeated until satisfactory values are obtained. With an ordinarily well-determined total pressure curve this should not be more than once.

The vapour pressures of solutions of the following compositions were determined:

Percentage by mass...	0·00	1·35	4·40	10·95	23·34	41·69	84·84	93·83
x	0·00	0·0024	0·0091	0·0215	0·0515	0·113	0·503	0·737

From these and the vapour pressures of water given by Landolt and Börnstein curves were constructed and the values of p_a and p_w calculated as indicated above. The values are given in Table I, as shown by curves in Figs. 1, 2, and 3. At 22°, so much of the curves

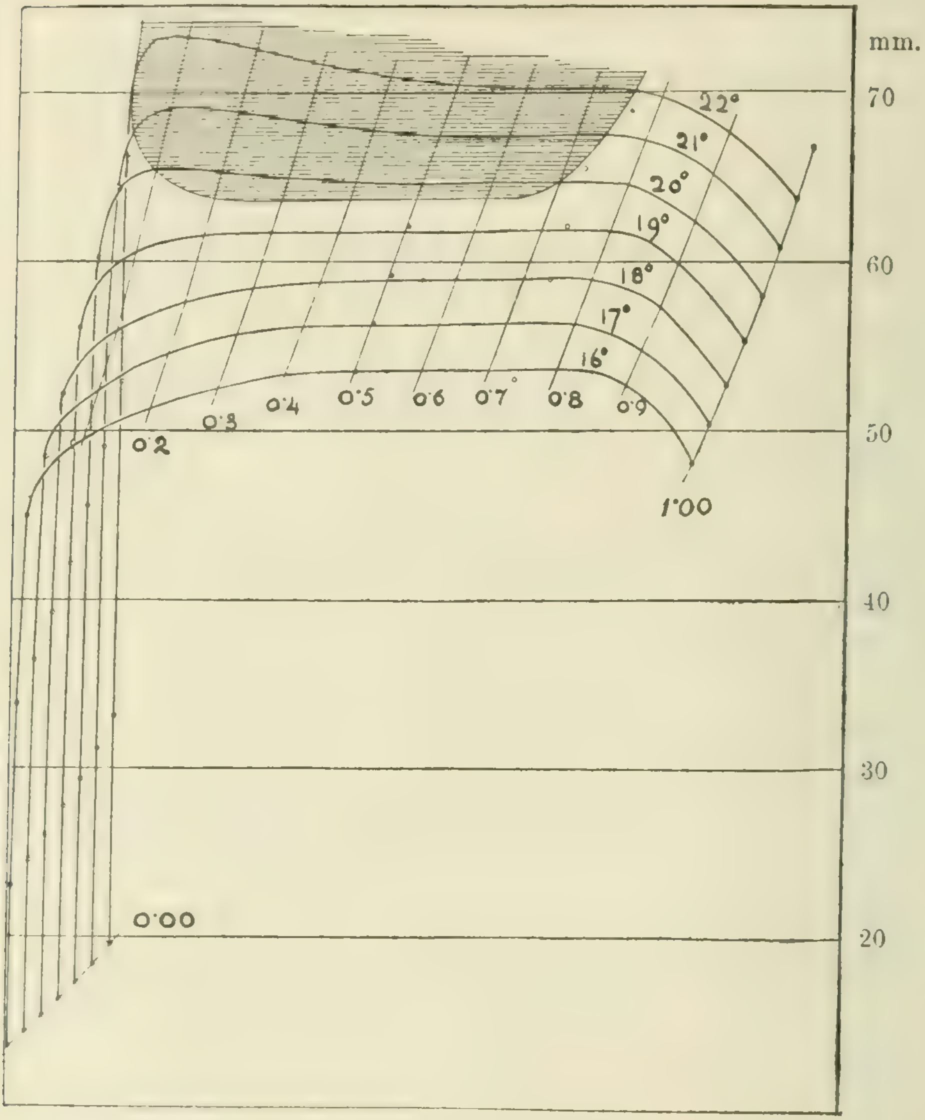
TABLE 1.

x.	16°.			18°.			20°.			22°.		
	π.	p_a.	p_w.	π.	p_a.	p_w.	π.	p_a.	p_w.	π.	p_a.	p_w.
0·00	13·585	0·00	13·585	15·383	0·00	15·383	17·406	0·00	17·406	19·66	0·00	19·66
0·05	47·50	34·30	13·20	54·10	39·25	14·85	64·25	47·40	16·85	73·18	53·84	19·34
0·10	49·43	36·36	13·07	56·00	41·20	14·80	65·36	48·66	16·70	73·18	53·82	19·36
0·15	50·42	37·45	12·97	56·92	42·185	14·735	65·29	48·53	16·76	72·84	53·44	19·40
0·20	51·30	38·42	12·88	57·60	42·91	14·69	65·16	48·37	16·79	72·415	52·97	19·445
0·25	52·00	39·225	12·775	58·065	43·44	14·625	65·05	48·22	16·83	72·015	52·53	19·485
0·30	52·60	39·92	12·68	58·435	43·85	14·585	64·925	48·08	16·845	71·635	52·08	19·555
0·35	53·04	40·44	12·60	58·645	44·12	14·525	64·82	47·95	16·87	71·27	51·64	19·63
0·40	53·32	40·80	12·52	58·795	44·29	14·505	64·715	47·82	16·895	70·935	51·20	19·735
0·45	53·48	41·035	12·445	58·84	44·37	14·47	64·635	47·71	16·925	70·61	50·75	19·86
0·50	53·53	41·14	12·39	58·89	44·42	14·47	64·58	47·63	16·95	70·405	50·42	19·985
0·55	53·56	41·18	12·38	58·91	44·475	14·435	64·54	47·56	16·98	70·25	50·20	20·05
0·60	53·59	41·235	12·355	58·95	44·535	14·415	64·55	47·56	16·99	70·23	50·11	20·12
0·65	53·62	41·29	12·33	58·975	44·605	14·37	64·56	47·60	16·96	70·23	50·15	20·07
0·70	53·65	41·37	12·28	59·015	44·70	14·315	64·595	47·69	16·905	70·25	50·22	20·03
0·75	53·67	41·53	12·12	59·03	44·82	14·21	64·60	47·90	16·70	70·18	50·45	19·73
0·80	53·67	41·79	11·88	58·95	45·23	13·72	64·50	48·60	15·90	69·65	51·76	17·89
0·85	53·50	42·31	11·19	58·40	46·42	11·98	63·50	50·45	13·05	68·76	54·61	14·15
0·90	52·50	43·62	8·88	57·20	48·00	9·20	62·25	52·71	9·54	67·10	57·53	9·87
0·95	51·10	45·80	4·70	55·30	50·20	5·10	60·50	55·20	5·30	66·00	60·58	5·12
1·00	48·20	48·20	0·00	52·77	52·77	0·00	57·96	57·96	0·00	63·70	63·70	0·00

falls within the unreal portion (indicated by shading) that the values had to be largely obtained by extrapolation.

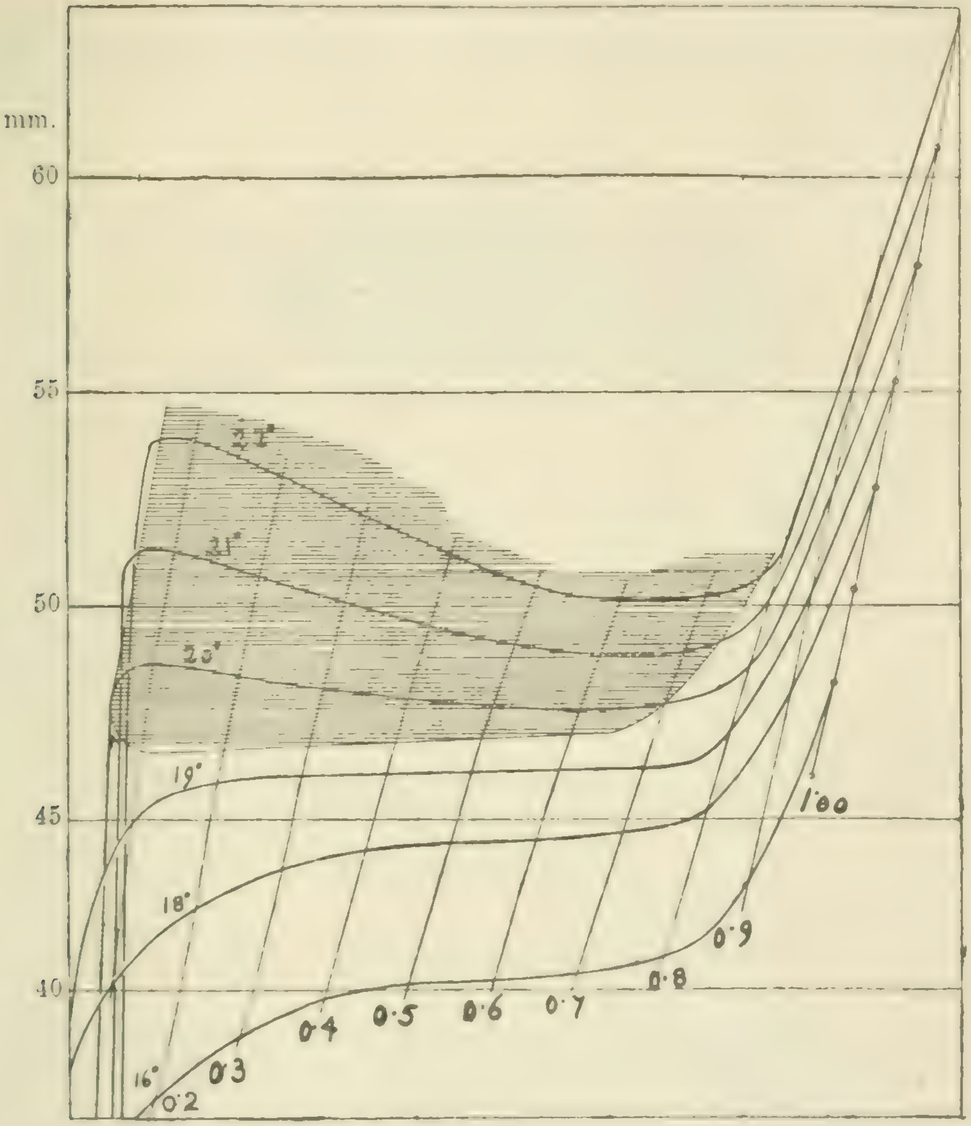
The gradual change in the type of the curves is obvious. At 16°, the total pressure curve is of the common single-maximum type, and the partial pressure curves are of Marshall's type 3; but as the temperature rises, the characters of the curves change, until at 19° a flat portion appears in all. Above 19° each partial pressure curve has both a maximum and a minimum point, and each total pressure curve has two maxima; there is consequently an unreal portion in every curve, and this increases in length as the temperature rises.

FIG. 1.—*Total Pressure Isotherms.*



If the total pressure is plotted against the composition of the vapour, instead of that of the liquid as is usual, the vapour-pressure curves (Roozeboom's "gas curves") assume the form shown in Fig. 4. As the unreal portion now assumes the form of a loop, it can readily be seen that the mixtures in equilibrium at 22° give a vapour the composition of which is given by $x = 0{\cdot}7226$, and the vapour pressure by 70·11 mm. This corresponds to liquids for which $x = 0{\cdot}772$ and 0·020.

FIG. 2.—*Partial Pressure of Amine Vapour.*



From each curve, similar values were read off and the following results obtained:

19°. All concentrations are possible.
20°. $x = 0{\cdot}699$ and 0·045. $\pi = 64{\cdot}60$ (64·45).* Composition of vapour $= 0{\cdot}7380$.

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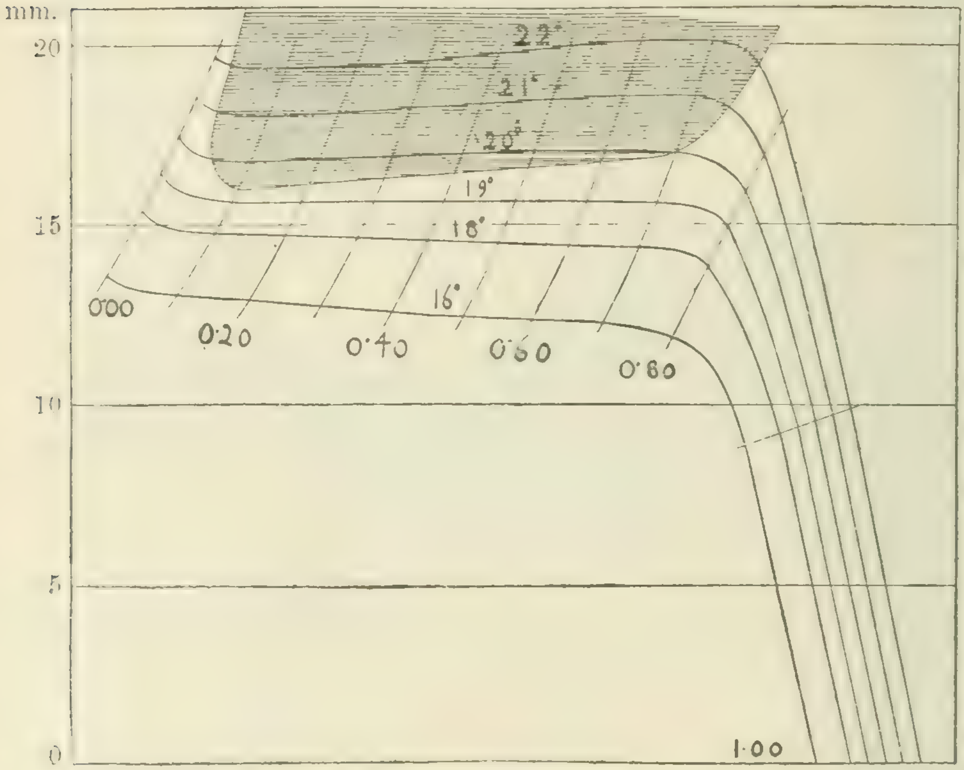
* The figures in brackets are the means of experimental values.

21°. $x = 0·737$ and 0·03. $\pi = 67·87$ (67·30). Composition of vapour
= 0·7333.
22°. 0·772 and 0·02 70·11 (70·71). Composition of vapour
= 0·7226.

It will be seen that the total pressure curve at 22° belongs to a slightly different type from that at 20°, since both the maxima at the higher temperature come within the unreal portion.

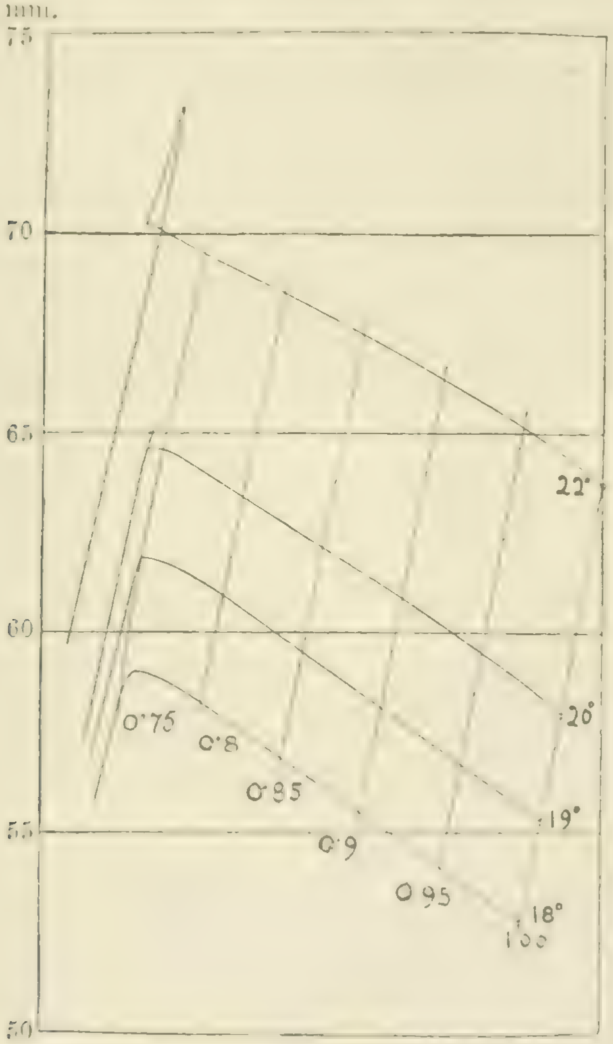
The values obtained from the equilibrium concentrations have been plotted against the temperature in Fig. 5. Some of Rothmund's and of Guthrie's direct observations on the separation of mixtures of triethylamine and water have been plotted in the same figure (*Zeitsch. physikal. Chem.*, 1898, **26**, 433; *Phil. Mag.*, 1884, [v], **18**, 500). The most serious discrepancies appear in the neighbourhood of $x = 0·1$. There are probably two reasons for this: (i) this is the region in which it is most difficult to obtain results from the vapour-pressure curves, and (ii) most of the observations are by Guthrie; now the remainder of his observations were shown by Rothmund (*loc. cit.*) to be, not only inaccurate, but impossible. From the curves, it will be seen that the vapours in contact with the equilibrium mixtures at 22° should have pressures $p_a = 50·66$ and $p_w = 19·45$. A direct determination of the partial pressure of the amine vapour was therefore made with

FIG. 3.—*Partial Pressure of Water Vapour.*



this mixture by the Earl of Berkeley and E. J. G. Hartley's modification of the bubbling method. The vapours carried over by 20 litres of air were passed through dilute sulphuric acid and so analysed. The values obtained for p_a were 50·07 and 51·38 mm. in two separate experiments giving for an average value 50·73 mm. The agreement is satisfactory considering the somewhat inaccurate calculation on which one result depends.

FIG. 4.



II. 2:4:6-*Trimethylpyridine.* (*γ-Collidine*).

The mutual solubilities of this compound and of water have been determined by Rothmund (*loc. cit.*). It was hoped that, since the mutual solubilities of water and trimethylpyridine are greater than those of water and triethylamine, this pair would prove more suitable for the purposes of this investigation. The extremely small vapour pressures of trimethylpyridine at the ordinary temperature rendered the results liable to large percentage errors and so unsuitable for mathematical analysis.

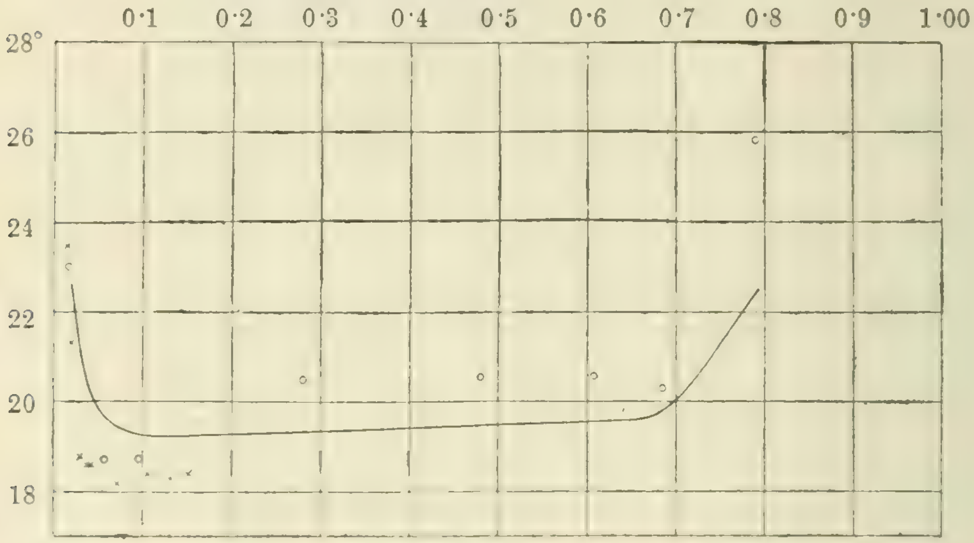
2 : 4 : 6-Trimethylpyridinedicarboxylic ester was prepared by Hantzsch's method (*Annalen*, 1882, **215**, 1) and simultaneously hydrolysed and deprived of the carboxylic groups by heating with soda-lime (Mai and Aschoff, *Ber.*, 1892, **25**, 374).

The total pressures of the solutions were determined in the same way as were those of triethylamine, with the exception of the solution for which $x = 0{\cdot}1745$, which was compared with pure water in a tensimeter.

The total pressure curves are of exactly the same type as those obtained for mixtures of triethylamine and water. The results of the measurements are given in Table 3.

As might have been expected, the isotherms for both triethylamine-water mixtures and for trimethylpyridine-water mixtures bear a striking resemblance to those obtained by Zawidzki for pyridine and water (*Zeitsch. physikal. Chem.*, 1900, **35**, 196), and to those obtained by Schreinemakers (*ibid.*, 474) for aniline-water mixtures.

Fig. 5.

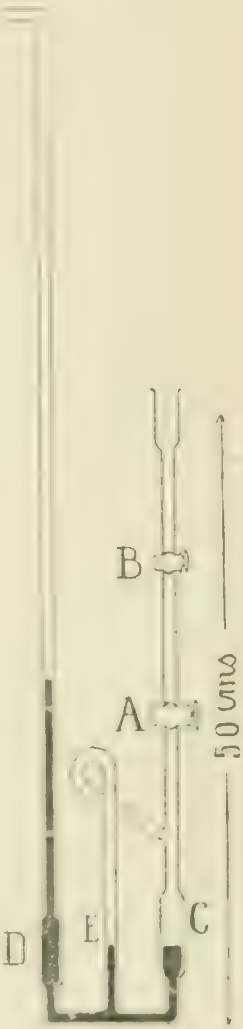


Experimental.

Total Pressures.

The apparatus used for determining total pressures is shown in Fig. 6. After being cleaned and dried, it was immersed to the level of the tap *B* in a bath having glass sides, and was sealed to a tube containing phosphorus pentoxide connected with a Töpler pump. The apparatus was then exhausted and left overnight with both taps closed. When it was judged that the inside of the apparatus was fairly dry, tap *B* was opened and mercury was poured in through the cup in slightly more than sufficient quantity to fill the tube between *B* and *A*. The cup was then exhausted through a tube passing through a rubber plug placed in the top of the cup. *B* was then closed, and by opening *A* part of the mercury above it was allowed to fall into the apparatus; this amount of mercury was not sufficient to "seal" the apparatus at the bottom. The pump was worked continuously. By this means a column of mercury free from bubbles was obtained in the lower part of the tube between *B* and *A*. The tap *B* was now opened, and air admitted to the cup, which was filled with mercury. By turning *A* and *B* alternately, it was possible to leave either mercury or a vacuum in the upper part of the tube between them. No considerable amount of air was thus carried into the bulb *C* by the mercury.

Fig. 6.



When sufficient mercury had been let in, the pump was stopped and air admitted to the bulb *D*. As the mercury rising in *C* passed the ┬-join, the tap *A* was turned and any air imprisoned above the mercury consequently driven into the space between *A* and *B*. *C* was then evacuated, and the operation repeated.

The liquid, the vapour pressure of which was to be measured, was then placed in the cup. Nearly all the mercury between *A* and *B* was allowed to run down into *C*, the liquid being then run into the space so evacuated. When the space between *B* and *A* was full of liquid, the tap *B* was closed, and a few drops of mercury poured into the tube above it. The liquid was then admitted to *C*, where it floated on the mercury surface.*

The difference in level of the mercury surfaces in *D* and *E* could then be read by means of a cathetometer and a glass scale.

This apparatus has three advantages over most similar apparatus for the same purpose. (i) Both mercury surfaces are read in tubes of the same gauge, and there is consequently no correction for capillarity; (ii) both surfaces are dry, and (iii) the surface in *E* alters very little in level when the mercury rises considerably in *D*; this greatly reduces the necessary number of readings.

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* Tap *B* was lubricated with vaselin and indiarubber; *A* was provided with mercury traps at both ends, and the tube between the taps was always partly filled with mercury while readings were being made.

TABLE II.

Vapour Pressures of Mixtures of Triethylamine and Water.

%	1·35.	4·40.	10·95.	23·34.	41·69.	84·84.	93·83.
x.	0·0024.	0·0091.	0·0215.	0·0515.	0·1128.	0·5029.	0·7368.
6°	—	—	—	24·15	—	—	—
7	—	—	—	25·85	—	—	32·89
8	14·94	—	—	27·67	—	—	34·68
9	15·66	20·02	25·97	29·61	—	—	36·59
10	16·43	21·58	28·07	31·69	33·26	—	38·57
11	17·23	23·25	30·49	33·93	35·47	41·54	40·65
12	18·25	25·07	33·25	36·31	37·90	43·41	42·83
13	19·36	27·01	35·89	38·84	40·32	45·63	45·15
14	20·56	29·10	38·71	41·57	42·98	48·14	47·63
15	21·82	31·36	41·70	44·47	45·74	50·79	50·23
16	23·15	33·79	45·01	47·57	48·65	53·56	53·02
17	24·57	36·42	48·50	50·88	51·66	56·38	55·89
18	26·08	39·25	52·27	54·20	54·93	59·25	58·93
19	27·69	42·30	56·19	57·65	58·49	62·16	62·13
20	29·41	45·59	60·28	61·30	62·23	65·62	65·50
21	31·23	49·12	64·45	65·13	65·93	69·20	69·06
22	33·16	52·94	68·83	69·15	69·78	72·92	72·85
23	35·22	57·05	72·77	73·37	73·75	76·94	76·58
24	37·43	61·50	76·85	77·77	77·84	80·78	80·49
25	39·77	66·22	81·14	82·37	82·03	84·98	84·61
26	42·25	71·29	85·65	87·18	86·49	89·31	88·92
27	44·88	76·67	90·22	—	91·12	93·84	93·48
28	47·69	81·39	94·98	—	95·99	98·56	98·25

%	1·35.	4 40.	10·95.	41·69.	84·84.	93·83.
x.	0·0024.	0·0091.	0·0215.	0·1128.	0·5029.	0·7368.
29°	50·71	87·46	100·19	101·02	103·48	103·27
30	53·97	95·88	105·17	106·24	108·62	108·52
31	57·36	100·66	110·60	111·74	113·99	114·01
32	61·00	107·81	116·28	117·52	119·62	119·71
33	64·78	115·32	122·27	123·54	125·49	125·67
34	68·81	123·22	128·57	129·82	131·65	131·84
35	73·04	131·57	135·09	136·37	138·08	138·27
36	77·47	140·19	141·86	143·18	144·80	144·91
37	82·19	148·55	148·82	150·19	151·84	151·82
38	87·10	156·48	156·08	157·42	159·19	158·97
39	92·31	164·47	163·68	164·87	166·85	166·42
40	97·77	172·78	171·54	172·55	174·80	174·15
41	103·55	181·14	179·79	180·47	183·03	182·22
42	109·60	189·74	188·31	188·72	191·55	190·61
43	115·82	198·70	197·09	197·36	200·36	199·33
44	122·31	207·83	206·28	206·38	209·45	208·40
45	129·06	217·54	—	215·79	218·83	217·35
46	136·02	—	—	—	—	227·67
47	143·33	—	—	—	—	—
48	150 94	—	—	—	—	—
49	158·85	—	—	—	—	—
50	167·17	—	—	—	—	—

The part of the table enclosed in heavy lines refers to temperatures at which the solubilities are only partial.

Observations were then made at intervals of about 0·2° at temperatures ranging between 7° and 50°; all sudden or rapid changes of temperature were avoided.

A complete set of observations was then smoothed by the use of the approximate equation:

$$At = \log.p - B,$$

where A and B are constants. A suitable value for B was chosen, and the values of A calculated for each observation separately. These values for A were then plotted against t on squared paper and a smoothed curve drawn. The values of A were then read off for each degree over the experimental range. The values for p thus calculated were corrected for the expansion of mercury.

In order to test the accuracy of the apparatus, two sets of observations were made with water. These gave the following results:

18·5°	16·40	(15·868)	13°	11·18	(11·187)
19	16·81	(16·167)	14	11·70	(11·936)
19·5	17·22	(17·880)	15	12·36	(12·728)
20	17·66	(17·406)	16	13·11	(13·565)
20·5	18·07	(17·947)	17	13·98	(14·450)
21	18·48	(18·503)	18	14·92	(15·383)
			19	16·06	(16·367)
			20	17·41	(17·406)

The figures in brackets are taken from Landolt and Bornstein's tables for comparison.

TABLE III.

Vapour Pressures of 2:4:6-Trimethylpyridine and its Solutions in Water.

Per cent.	6.	52·90.	58·65.	85·74.	95·8.	98·7.	100
x.	0·0094.	0·143.	0·1745.	0·472.	0·7715.	0·9185.	1·000.
10°	9·1	9·8	—	—	—	—	2·7
15	12·7	13·0	13·1	—	10·4	7·9	3·3
20	18·2	17·6	17·85	17·5	14·3	10·9	4·1
25	24·6	24·2	24·1	14·4	19·3	15·1	5·2
30	33·1	32·3	32·3	32·9	26·6	20·8	6·3
35	44·2	43·4	42·9	43·2	36·1	28·7	7·7
40	57·7	56·3	56·45	57·0	49·0	38·1	9·4
45	74·8	74·1	73·6	74·8	65·6	50·5	11·7
50	96·4	95·2	95·0	96·0	85·8	67·2	14·8
55	122·3	120·9	121·9	124·0	111·5	87·4	18·9
60	—	—	—	—	—	—	23·8
65	—	—	—	—	—	—	31·0

The part of the table enclosed in heavy lines refers to temperatures where the solubilities are only partial.

The apparatus was taken down, set up as before, and similar experiments were made with triethylamine (Kahlbaum) freshly distilled from potash (b. p. 88·2—88·4° under 747·8 mm. pressure). The results are given on p. 1971. Solutions of various cencentrations were examined; the vapour pressures of these are given in Table II.

Partial Pressure.

The partial pressure of triethylamine over the equilibrium mixture at 22° was measured by a slight modification of the Earl of Berkeley and E. J. G. Hartley's method (*Proc. Roy. Soc.*, 1906, **77**, 150). Air freed from carbon dioxide and moisture by passing through towers containing potash and soda-lime was drawn through three weighed tubes containing (i) the amine-water mixtures, (ii) 30 c.c. of 2·516*N*-sulphuric acid, and (iii) concentrated sulphuric acid. The tubes were shaken in a thermostat in such a way that their inner surfaces were continuously wetted with the contained liquid.

When the aspirator, which held 20 litres, was empty of water, the tubes were removed, disconnected, washed, and left with stoppers in a box containing trays of calcium chloride. They were subsequently weighed.

The dilute acid in tube (ii) was then washed out and titrated with *N*-sodium carbonate solution. From this the mass of amine carried over by the air could be calculated. From the difference between this weight and the loss in weight of the tube (i)—or the united gains of (ii) and (iii)—the mass of water vapour could be obtained. The shape of the tubes makes accurate weighing on an ordinary balance impossible; even when the tube can be placed on the pan it is liable to tilt, owing to the flow of liquid to one end (Berkeley and Hartley used a specially constructed balance). In making the calculations, it has been assumed that the partial pressure of water vapour over these solutions is 19·42 mm. at 22°. If the vapour pressure of the water is entirely neglected, the pressure calculated for the amine vapour will be raised by 1·26 mm.; an error of several millimetres in the value assumed for p_w will not therefore make a very serious error in p_a.

Two experiments were made and yielded the following results:

Mass of amine, in grams.	Volume of air, in litres, corrected to N.T.P.	Height of barometer in mm.	Duration of experiment, in hours.	p_a.
6·301	18·624	756	16·5	51·385
6·1013	18·460	753	21·5	50·073

In the second experiment, tubes (i) and (ii) were partly filled with hollow glass beads.

The mean result is $p_a = 50·73$ mm.

My heartiest thanks are due and gratefully rendered to Dr. H. Brereton Baker and the Governing Body for allowing me to carry out these experiments in Christ Church laboratory.

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CXCII.—*Liquid Triethylamine.*

By ROBERT TABOR LATTEY.

THE molecular latent heat of triethylamine calculated from the vapour pressure and its rate of change with change of temperature give values rising from 7100 Cal. at 14° to 8160 Cal. at 49°. In the case of most liquids, the latent heat decreases with rising temperature; anomalous behaviour is noticed in the case of acetic acid (Roozeboom, *Heterogene Gleichgewichte*, I, 52), and indicates a difference in the composition of the gaseous and liquid phases.

The rise in the case of triethylamine is small (see Table I) and might easily be due to experimental errors. It seemed, however, worth while to investigate some of the properties more closely in order to determine which of the two explanations was the more probable.

TABLE I.

Temp.	Vapour pressure.	dP/dT.	$q \times 10^{-2}$.	Temp.	Vapour pressure.	dP/dT.	$q \times 10^{-2}$.
10°	37·37	—	—	31°	96·30	4·295	80·8
11	38·82	1·515	61·7	32	100·69	4·465	80·8
12	40·40	1·655	65·1	33	105·23	4·605	80·3
13	42·13	1·795	68·2	34	109·90	4·785	80·4
14	43·99	1·93	70·8	35	114·80	4·97	80·5
15	45·99	2·06	72·8	36	119·84	5·15	80·5
16	48·11	2·19	74·5	37	125·10	5·355	80·6
17	50·37	2·33	76·2	38	130·55	5·55	80·7
18	52·77	2·465	77·5	39	136·20	5·75	80·6
19	55·30	2·595	78·4	40	142·05	6·00	81·1
20	57·96	2·73	79·2	41	148·20	6·25	81·5
21	60·76	2·87	80·0	42	154·55	6·45	81·2
22	63·70	3·005	80·4	43	161·1	6·725	81·7
23	66·77	3·135	80·6	44	168·0	6·95	81·5
24	69·97	3·265	80·6	45	175·0	7·2	81·5
25	73·30	3·40	80·7	46	182·4	7·45	81·5
26	76·77	3·545	80·9	47	189·9	7·725	81·6
27	80·39	3·685	80·8	48	197·85	8·00	81·6
28	84·14	3·825	80·7	49	205·9	8·275	81·6
29	88·04	3·98	80·8	50	214·4	—	—
30	92·10	4·13	80·6				

In Table II are compared the vapour pressures of triethylamine,

TABLE II.

	Vapour pressures at corresponding temperatures $= P$.				P/P_{κ}.			
	Hexane.	Amine.	Alcohol.	Water.				
T/T_{κ}.	$T_{\kappa} = 234{\cdot}8^{\circ}$.	$267{\cdot}1^{\circ}$.	$243{\cdot}6^{\circ}$.	$358{\cdot}1^{\circ}$.	Hexane.	Amine.	Alcohol.	Water.
1·000	22510	22800	48900	118580	1·0000	1·0000	1·0000	1·0000
0·670	720·4	760	606	3581	0·0320	0·0333	0·0124	0·0241
0·598	184·4	214·4	130	875·6	0·0082	0·0094	0·0027	0·0059
0 577	119·42	136·2	59·4	545·8	0·0053	0·0060	0·0012	0·0037
0·557	74·67	84·1	32·0	336·5	0·0033	0·0037	0·00066	0·0023
0·538	44·92	50·4	17·5	195	0·0020	0·0022	0·00036	0·0013

hexane, ethyl alcohol, and water. The necessary data were obtained from Landolt and Börnstein's tables. When the values of the ratio of the vapour pressure to the critical pressure for the amine are compared with the ratios obtained at corresponding temperatures for the other three liquids, it is at once clear that the behaviour of triethylamine is far more nearly akin to that of the unimolecular hexane than to that of either of the typical associated liquids, alcohol and water.

A comparison of the molecular latent heats, q, at various temperatures with those of other liquids at corresponding temperatures leads to the same conclusion.

The values are given in Table III, and were calculated from the

TABLE III.

	Hexane.		Amine.		Alcohol.		Water.	
T/T_{κ}.	$q \times 10^{-2}$.	q/T.	$q \times 10^{-2}$.	q/T.	$q \times 10^{-2}$.	q/T.	$q \times 10^{-2}$.	qT.
0·670	72·1	21·1	—	20·0	—	26·4	—	—
0·598	74·6	24·6	81·6	25·25	—	—	95·9	25·4
0·577	75·3	25·7	80·6	26·7	100·7	33·8	97·6	26·8
0·557	75·8	26·8	80·7	26·8	98·0	34·0	99·3	28·2
0·538	76·4	28·0	76·2	26·3	95·0	34·2	100·3	29·7

formula: $\frac{dP}{dT} = \frac{0{\cdot}5102Pq}{T^2}$, except in the case of water. These results were confirmed by an examination of the molecular surface energy. The surface tensions of triethylamine at 11° and at 30° were compared with those of water at the same temperatures by comparing the pressures necessary to force a bubble of air from a capillary opening immersed in the fluid (Whatmough, *Zeitsch. physikal. Chem.*, 1901, **39**, 129). In connexion with these experiments, my thanks are due to Mr. H. B. Hartley, of Balliol College, for kindly placing at my disposal his apparatus for these determinations and also for much kind help.

Taking the surface tensions of water at 11° and 30° as 71·83 and 69·10 dynes per sq. cm. respectively (Landolt and Börnstein), the following results were obtained for triethylamine.

$\gamma_{11°}$	$\gamma_{30°}$	$\gamma_{11°}$	$\gamma_{30°}$
27·71	25·13	27·61	25·34
28·08	25·47	27·25	25·05
27·76	25·61		
	Mean ……	27·70	25·37

The molecular volumes for these temperatures were calculated from the density determinations made by Sir W. H. Perkin (Trans., 1889, **55**, 692) as 137·12 and 139·32 respectively. From these the molecular surface energies, $a = \gamma v^{\frac{2}{3}}$, were calculated to be 736·4 at 11° and 681·7 at 30°. The temperature coefficient, $\frac{da}{dt}$, is therefore 2·879, and the mean critical temperature calculated by Ramsay and Young's method is $\frac{681·7}{2·879} + 30° + 6° = 272·8°$. Pawlewski (*Ber.*, 1883, **16**, 2633) gives 267·1°, and Vincent and Chappuis (*Compt. rend.*, 1886, **103**, 379) give 259° for the value of T_K.

Since associated liquids give values for $\frac{da}{dt}$ less than 2·121, it is improbable that triethylamine is associated.

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CXCIII.—*The Alcohols of the Hydroaromatic and Terpene Series. Part I. Resolution of the Alcohols into their Optically Active Components and the Preparation of the Borneols.*

By Robert Howson Pickard and William Oswald Littlebury.

Introduction.

Several of the problems still awaiting solution in the terpene and hydroaromatic series are connected with the alcohols of this class of compounds. Such, for example, are the questions of the relation of borneol to *iso*borneol; of fenchol to *iso*fenchol; between the various "camphenes" and "fenchenes"; between the various menthols; and also the problem of the isolation in a pure state and determination of the constitution of the stereoisomerides formed in the reduction of the phenols by the splendid catalytic method of Sabatier and Senderens.

The confusion existing in the literature on several of these questions appears to us to be caused partly by investigations carried out with impure materials. Now, since nearly all the alcohols in question are either optically active or contain one or more asymmetric carbon atoms in the molecule, it is obvious that the first step in a re-investigation of these problems is to discover a method, or methods, which will allow of the purification of the alcohols with regard to their specific rotation, and also of the resolution of the synthetic or otherwise inactive compounds into their optically active components.

Such a method, it was hoped, would be the preparation and fractional crystallisation of the *l*-menthylcarbamates previously described by us (Trans., 1904, **85**, 685; 1906, **89**, 93, 467, 1254). This method, however, is not always applicable; thus, to take a few examples, the *d*- and *l*-*iso*bornyl *l*-menthylcarbamates, prepared from *iso*borneol (from "camphene") and *l*-menthylcarbimide, seem to form mixed crystals inseparable by fractional crystallisation, whilst the *l*-menthylcarbamate of 1 : 3-methyl*cyclo*hexanol is a viscous oil.

The problem has been solved in a more simple manner, and the alcohols can be resolved into their optically active components by the method described below, which appears to be quite a general one, for it has been applied, not only in the cases indicated above, but also to alcohols of simpler constitution. There are three stages in the process. Firstly, the alcohol is converted into the hydrogen ester of a polybasic acid by heating with the anhydride of the same. For this purpose, phthalic and succinic anhydrides are well adapted, and in some cases the compounds required have been already described, for example, the bornyl hydrogen phthalates (Haller, *Compt. rend.*, 1889, **108**, 456) and *β*-thymomenthyl hydrogen phthalate (Brunel, *Compt. rend.*, 1905, **140**, 252). Secondly, these acid esters, for example, $CO_2H\cdot C_6H_4\cdot CO_2R$, are resolved by a strong optically active base, according to Pasteur's method. In some cases, the commoner alkaloids suffice for the purpose, in others it is necessary to use *l*-menthylamine, which is a strong base and very serviceable for the resolution of weak acids, as has been pointed out by one of us and collaborators (Trans., 1905, **87**, 1763; 1906, **89**, 384 and 1101). Thirdly, the pure optically active acid ester is hydrolysed. The hydrolysis is, as a rule, easily effected by warming with the calculated amount of alcoholic sodium hydroxide, or even by merely boiling an aqueous solution of the sodium salt of the acid ester (compare Haller, *loc. cit.*). The ease with which this third stage is accomplished renders this new method preferable to our first method, since some of the *l*-menthylcarbamates are only hydrolysed with extraordinary difficulty under conditions tending to racemisation. The new method, moreover, has the further advantage in that it allows of the preparation of the two components, whereas the menthylcarbimide method generally yields only the one.

The underlying idea of the method does not seem altogether new, for Krüger (*Ber.*, 1893, **26**, 1203) appears to have attempted, unsuccessfully, the resolution of methylpropylcarbinyl hydrogen sulphate by means of the strychnine salt, whilst, during the course of this work, Meth (*Ber.*, 1907, **40**, 695) described a resolution of *sec.*-butyl alcohol by an analogous method. Meth's process includes the preparation of a hydrogen sulphuric ester, and the use of sulphuric acid is, of course, quite impossible, except in the case of the most stable alcohols, on account of its strong dehydrating action.

The present communication describes the preparation of *d*- and *l*-borneol and *d*- and *l*-*iso*borneol, and, it is hoped, will be followed shortly by others dealing with the problems indicated above.

Borneol and iso*Borneol.*

d- and *l*-Borneols were prepared in a state of purity by Haller, and described by him under the name of camphols (*Ann. Chim. Phys.*, 1885, [vi], **27**, 424). Recently, the separation of these from other isomerides (*iso*borneols) has been described by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1096), who showed that the methyl bornylxanthates, but not the *iso*bornyl esters, when hydrolysed, gave the corresponding alcohols. The borneols described by Tschugaeff had a slightly higher rotation than those of Haller. We have prepared pure borneols by three methods, each of which yielded products of practically identical rotation to those given by Haller. These are: (i) by Tschugaeff's method; (ii) by fractional crystallisation and subsequent hydrolysis of *l*-bornyl *l*-menthylcarbamate, and (iii) by similar treatment of the *l*-menthylamine salts of *d*- and *l*-bornyl hydrogen phthalates.

*iso*Bornyl hydrogen phthalate is readily prepared by the action of phthalic anhydride on the inactive *iso*borneol obtained by the hydrolysis of its acetate, which is formed when camphene is treated with acetic and sulphuric acids (Bertram and Walbaum, *J. pr. Chem.*, 1894, [ii], **49**, 15). It is readily resolved by *l*-menthylamine, the *lBdA*-component being less soluble in dilute alcohol; whilst the optical antipode is obtained by crystallising the *d*-cinchonine salt, when the *dBlA*-component is the less soluble in alcohol. From these salts, the *d*- and *l*-*iso*bornyl hydrogen phthalates have been obtained, and, when hydrolysed, yield the pure *d*- and *l*-*iso*borneols. These have specific rotations approximately $[\alpha]_D \pm 34{\cdot}3^\circ$ in ethyl-alcoholic solution, and when oxidised give pure camphor with a specific rotation of opposite sign. Haller's *iso*camphols had $[\alpha]_D \pm 32{\cdot}9°$ in ethylalcoholic solution.

Our results therefore confirm Haller's work on the camphols, and prove the truth of the suggestion (Bertram and Walbaum, *loc. cit.*) that his *iso*camphols are identical with *iso*borneol. We would, however, point out that it is by no means certain that "*iso*borneol," prepared from camphene, contains only *d*- and *l*-*iso*borneols. The method described in this paper allows of the easy preparation of the pure *iso*borneols in quantity, and will afford material for the reinvestigation of the relationship between borneol and its isomeride.

EXPERIMENTAL.

Borneol.—The crude *l*-borneol used in our experiments was obtained from Schimmel, and after one crystallisation from light petroleum had $[\alpha]_D - 37{\cdot}1°$ in toluene with $c^* = 11{\cdot}5$. Fifty grams of this were converted by Tschugaeff's method (*loc. cit.*) into methyl *l*-bornylxanthate, $CH_3{\cdot}S{\cdot}CS{\cdot}O{\cdot}C_{10}H_{17}$.

The ester was distilled with steam and, after two crystallisations from dilute alcohol, melted at 58°. The borneol obtained from this product by hydrolysis with alcoholic sodium hydroxide was distilled with steam and crystallised from light petroleum. 2·3021 gram, made up to 19·9 c.c. with toluene, gave $\alpha_D - 8{\cdot}77°$, whence $[\alpha]_D - 37{\cdot}91°$ ($c = 11{\cdot}5$). Tschugaeff gives $[\alpha]_D - 38{\cdot}23°$ ($c = 13{\cdot}12$).

Purification of l-*Borneol by Means of* l-*Menthylcarbimide.*

l-*Bornyl* l-*Menthylcarbamate*, $C_{10}H_{19}{\cdot}NH{\cdot}CO_2{\cdot}C_{10}H_{17}$.

Molecular quantities of *l*-menthylamine, *l*-bornyl chlorocarbonate,[†] and sodium hydrogen carbonate are mixed in toluene and heated on a water-bath for three hours. The toluene solution, after washing with water and dilute hydrochloric acid, is distilled and the residue crystallised from dilute alcohol. After two crystallisations from dilute alcohol, the pure substance was obtained in long, colourless, prismatic rods, which melted at 136°:

0·3688 gave 15·0 c.c. moist nitrogen at 18° and 747 mm. N = 4·3.

$C_{21}H_{37}O_2N$ requires N = 4·2 per cent.

The specific rotation of the crude product was $[\alpha]_D - 67{\cdot}0°$ in ethylalcoholic solution, and this, during the fractional crystallisation, in-

---

[*] c = number of grams of substance in 100 c.c. of solution. All rotations recorded in this paper were observed in a 2-dcm. tube at 15—18°.

[†] Bornyl chlorocarbonate, b. p. 130°/35 mm., is readily prepared by heating borneol dissolved in toluene with the addition compound of carbonyl chloride and antipyrine (compare D.R.-P. 1901, 117624).

creased to the constant value $[\alpha]_D$ $-71\cdot04°$ (with c between 2·5 and 4·3), whence $[M]_D$ $-238\cdot0°$.

Hydrolysis of l-*Bornyl* l-*Menthylcarbamate.*—The carbamate was hydrolysed under varying conditions. Two experiments only are here recorded. In the first, a large excess of sodium hydroxide was used; in the second, $1\frac{3}{4}$ mol. only (2 molecules being theoretically required for complete hydrolysis). In each of these, the ester was heated in a sealed tube with the alcoholic sodium hydroxide for five hours at about 140°. The alcohol was then evaporated, the residue acidified, and the *l*-borneol distilled in a current of steam. After crystallisation from light petroleum, the specific rotations of the products from the two experiments were determined:

From (1): 2·3149, made up to 19·9 c.c. with toluene, gave $\alpha -8\cdot85°$, whence $[\alpha]_D$ $-37\cdot96°$ ($c = 11\cdot5$).

From (2): 2·3049, made up to 19·95 c.c. with toluene, gave $\alpha -8\cdot76°$, whence $[\alpha]_D$ $-37\cdot92°$.

Purification of l-*Borneol by Means of the* l-*Menthylamine Salt of Bornyl Hydrogen Phthalate.*

The l-*menthylamine* salt of bornyl hydrogen phthalate is readily obtained when an aqueous solution of *l*-menthylamine hydrochloride (1 mol.) is added to a neutral solution of the phthalate (1 mol.) in a solution of potassium carbonate. The precipitated pasty mass soon hardens, and, after four crystallisations from dilute methyl alcohol, the salt is obtained in prismatic needles, melting at 160°, with a constant specific rotation in methyl alcohol of $[\alpha]_D$ $-52\cdot8°$ with $c = 5\cdot0$. The salt is decomposed by dilute hydrochloric acid, and the resulting *l*-bornyl hydrogen phthalate hydrolysed by boiling with alcoholic sodium hydroxide. The *l*-borneol thus obtained was crystallised once from light petroleum, and had $[\alpha]_D$ $-37\cdot61°$ in toluene solution with $c = 8\cdot0$.

d-*Borneol from the Reduction Products of Camphor.*

Natural *d*-borneol is not readily obtainable. It may, however, be prepared from the commercial synthetic product prepared by the reduction of camphor. This seems to be composed of mixed crystals of *d*-borneol and l-*iso*borneol, and has $[\alpha]_D$ about $+24°$ in ethyl-alcoholic solution. Pure *d*-borneol can be obtained from it by the following method (compare McKenzie, this vol., 1225): 100 grams of the commercial product are dissolved in 80 grams of benzene, and boiled with 50 grams of zinc chloride for three hours. The solution is then washed with acidified water and fractionally distilled. The *d*-borneol thus obtained, after one crystallisation from light petroleum, has $[\alpha]_D$ +36·4° in ethyl-alcoholic solution, and can be further purified by conversion into the hydrogen phthalic ester and its *l*-menthylamine salt in the manner described above for *l*-borneol.

d-Bornyl hydrogen phthalate crystallises readily from glacial acetic acid in prismatic needles, and melts at 164°:

1·0069, made up to 19·85 c.c. with ethyl alcohol, gave α +5·75°, whence $[\alpha]_D$ +56·7°.

The l-*menthylamine* salt crystallises readily from acetone, and has $[\alpha]_D$ +17·2° in ethyl-alcoholic solution with $c = 5·0$.

The *d*-borneol, obtained by the hydrolysis of this ester, was unaltered in specific rotation by crystallisation from light petroleum. Of the three following polarimetric observations, (1) and (2) were carried out in ethyl alcohol, (3) in toluene; (1) with a product obtained by steam distillation, (2) and (3) with the recrystallised product:

(1) 1·3748, made up to 19·95 c.c., gave α + 5·11°, whence $[\alpha]_D$ +37·08°.

(2) 1·3749, made up to 19·85 c.c., gave α + 5·13°, whence $[\alpha]_D$ +37·03°.

(3) 2·3056, made up to 20 c.c., gave α + 8·71°, whence $[\alpha]_D$ +37·77°.

d- and l-iso*Borneol.*

The commercial product (from camphene) supplied to us by Schimmel and Co. was well crystallised, apparently homogeneous, and had a slight lævorotation ($[\alpha]_D$ −0·8° in ethyl alcohol). It is readily converted into the hydrogen phthalic ester by heating with phthalic anhydride for eight hours at 115—120°. The inactive *iso*bornyl hydrogen phthalate thus obtained crystallises in stellate clusters of prisms from glacial acetic acid, and melts at 168°.

l-*Menthylamine* d-iso*Bornyl Hydrogen Phthalate.*—The inactive ester (1 mol.) is dissolved in the calculated amount of a cold solution of sodium carbonate, and the solution precipitated with a cold aqueous solution of *l*-menthylamine hydrochloride (1 mol.). The resulting pasty mass soon hardens, and is then repeatedly crystallised from dilute alcohol. The first crop of crystals melts at 105—109°, and has $[\alpha]_D$ about −6° in ethyl alcohol ($c = 5·0$). The mother liquor from these is worked up as described below. The crystalline product after some seven or eight recrystallisations melts indefinitely at 116—118°, and has the specific rotation, which is unaltered by further recrystallisation, $[\alpha]_D$ +29·29° in ethyl alcohol ($c = 5$). The impure salt crystallises in clear, colourless, nodular clusters of prismatic needles; as the purification proceeds, however, the crystals, while of the same habit, become more dense and opaque. The salt was analysed, and gave results in agreement with the formula: $C_{10}H_{17}\cdot CO_2\cdot C_6H_4\cdot CO_2H,C_{10}H_{19}\cdot NH_2$.

d-iso*Bornyl Hydrogen Phthalate.*—The menthylamine salt was dissolved in warm glacial acetic acid and poured into water, the precipitated hydrogen ester being twice crystallised from glacial acetic acid. The compound was thus obtained in small, rectangular prisms melting at 167°. A polarimetric observation gave the following result:

1·0327, made up to 20 c.c. with chloroform, gave α +7·94°, whence $[\alpha]_D$ +76·88°.

d-iso*Borneol.*—The phthalate was heated for two hours on the water bath with the calculated amount of alcoholic sodium hydroxide, and the *iso*borneol separated from the solution by distillation with steam. A determination of the specific rotation of this product gave the following result:

1·0228, made up to 20 c.c. with ethyl alcohol, gave α +3·48°, whence $[\alpha]_D$ +34·02°.

After recrystallisation from light petroleum, the rotation was unaltered:

1·0951, made up to 19·9 c.c. with ethyl alcohol, gave α +3·75°, whence $[\alpha]_D$ +34·08°.

4·2025, made up to 20 c.c. with ethyl alcohol, gave α +14·33°, whence $[\alpha]_D$ +34·09°.

The specific rotation in toluene solution was determined:

2·3034, made up to 20 c.c. with toluene, gave α +4·91°, whence $[\alpha]_D$ +21·32°.

The melting point of the crystallised product was 214°, being 4° above the melting point of the product obtained from Schimmel.

The *l*-camphor, obtained from this by oxidation with nitrous fumes in chloroform solution, gave the following result in the polarimeter:

1·1118, made up to 19·9 c.c. with ethyl alcohol, gave α −4·72°, whence $[\alpha]_D$ −42·25°.

A specimen of pure sublimed camphor at the same concentration gave $[\alpha]_D$ +42·38°.

The rotation of the *d-iso*borneol was unaltered by distillation with steam from a strong solution of sodium hydroxide. Further proof that the product had not been racemised during the hydrolysis was obtained by reconverting it into the hydrogen phthalate, which had $[\alpha]_D$ +76·4°.

d-*Cinchonine* l-iso*Bornyl Hydrogen Phthalate.*—The mother liquor from the first crop of crystals of the menthylamine salt (see p. 1978) is poured into dilute acetic acid. The precipitated acid is then dissolved in alcohol and heated on the water-bath with the calculated quantity of cinchonine.* The base gradually dissolves, and, when cool, the crude salt is deposited in hard, nodular crystals, which melt indefinitely at 192—195°, and have $[\alpha]_D$ about $+55°$ in ethyl alcohol ($c=5$). After five or six recrystallisations from alcohol, the salt has a constant rotation and melts at 206°:

0·3706 gave 16·6 c.c. moist nitrogen at 20° and 750 mm. $N=5·0$.

$C_{10}H_{17}·CO_2·C_6H_4·CO_2H·C_{19}H_{22}ON_2$ requires $N=4·9$ per cent.

0·8762, made up to 20 c.c. with ethyl alcohol, gave α $+3·79°$, whence $[\alpha]_D$ $+43·25°$.

l-iso*Bornyl Hydrogen Phthalate.*—The cinchonine salt is decomposed in an analogous manner to the *l*-menthylamine salt. The resulting *l-iso*bornyl hydrogen phthalate crystallises from glacial acetic acid in hard nodules and melts at 167°:

1·0100, made up to 20 c.c. with chloroform, gave α $-7·77°$, whence $[\alpha]_D$ $-76·93°$.

When hydrolysed by heating for two hours with alcoholic sodium hydroxide (2½ mols.), it yields l-iso*borneol*, which was separated from the mixture by distillation with steam and gave the following result in the polarimeter:

0·7232, made up to 20 c.c. with ethyl alcohol, gave α $-2·50°$, whence $[\alpha]_D$ $-34·57°$.

After crystallisation from light petroleum, it melts at 214°. A determination of the specific rotation gave the following result:

1·0777, made up to 20 c.c. with ethyl alcohol, gave α $-3·70°$, whence $[\alpha]_D$ $-34·34°$.

dl-iso*Bornyl* l-*menthylcarbamate*, $C_{10}H_{19}·NH·CO_2·C_{10}H_{17}$, was prepared by methods analogous to those described under borneol. The compound crystallised in beautiful, glistening, prismatic needles, and was recrystallised five times from dilute alcohol. The melting point of the product was indefinite, being about 120°, but the rotation remained practically unaltered, being $[\alpha]_D$ $-55·8°$ and $[M]_D$ $-187°$ in ethyl-alcoholic solution with $c=5$; thus indicating that no resolution had been effected. The two carbamates were, however, prepared from the pure *iso*borneols by heating with *l*-menthylcarbimide for twelve hours at 120°.

d-iso*Bornyl* l-*menthylcarbamate* crystallises from alcohol in stout prisms melting at 128°:

0·5293, made up to 19·85 c.c. with ethyl alcohol, gave α $-0·75°$, whence $[\alpha]_D$ $-1·41°$.

l-iso*Bornyl* l-*menthylcarbamate* crystallises from dilute alcohol in small, prismatic needles melting at 118°, and is much more soluble in organic media than the corresponding *dl*-compound:

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* Experiments were made with less than the calculated quantity of the base with a view to effecting a quicker resolution, but gave no more advantageous results.

0·5276, made up to 20 c.c. with ethyl alcohol, gave α $-5{\cdot}91°$, whence $[\alpha]_D$ $-112{\cdot}0°$.

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CXCIV.—*The Interaction of Metallic Sulphates and Caustic Alkalis.*

By Spencer Umfreville Pickering, M.A., F.R.S.

The ultimate action of caustic alkalis on boiling solutions of sulphates of the heavy metals results, as is well known, in the precipitation of the metal as oxide or hydroxide, but it is only in a very few cases that any knowledge exists as to the product of the reaction at the ordinary temperature, although a basic sulphate is generally held to be formed, and many such basic sulphates have been isolated by various methods of procedure (see Habermann, *Monatsh.*, 1884, **5**, 442; Gorgeu, *Compt. rend.*, 1882, **94**, 1425; Pickering, Trans., 1880, **37**, 807; *Chem. News*, 1882, **45**, 121, and 1883, **47**, 181). For the purposes of an investigation to be described subsequently, it became necessary to ascertain the composition of these precipitates in the case of iron and copper, and the results thus obtained have been supplemented by an examination of the sulphates of other metals.

The examination was made by ascertaining the amount of alkali, generally either sodium or calcium hydroxide, required for the complete precipitation of the metal, and also the amount required to produce an alkaline reaction, using phenolphthalein as indicator.

The precipitates are all of a bulky and flocculent nature, and the completion of the precipitation cannot be ascertained by allowing them to settle, and then adding more of the alkali: filtration is necessary; and the method which had to be adopted was to add various quantities of the alkali to similar quantities of the sulphate, and ascertain by successive approximations the amount of alkali necessary to ensure complete precipitation. In some cases, of course, this can be ascertained by the use of a more delicate test than the addition of more alkali.

Weak solutions were used in all cases, their strength being about one gram-molecule in 100 litres.

The general character of the reaction appears to be similar with all the metallic sulphates examined, and with all the caustic alkalis. The metal is first precipitated as a basic sulphate of definite composition, which, on the addition of more alkali, is converted into a second, more highly basic sulphate, before any alkaline reaction becomes evident in the liquid. In some cases, the transformation takes place in two distinct stages.

In every instance examined, the products of the reaction, so far as the basicity of the precipitates is concerned, are the same, whether soda or lime be used, but the precipitates are not always identical in other respects, and this has been ascertained to be due to the fact that, when lime is used, they retain a considerable amount of the calcium sulphate formed in the reaction. The basicity of the products will, however, alone be discussed at present.

Copper Sulphate.

The basic sulphates of copper were investigated by the author in 1883 (*Chem. News*, **47**, 181), and it was ascertained that two such existed in definite form: $3CuO,SO_3$, obtained by boiling a solution of copper sulphate, and $4CuO,SO_3$, obtained (*a*) by precipitating copper sulphate solutions with an amount of potash not exceeding 0·75 equivalent; (*b*) by decomposing the sulphate with an acetate, or (*c*) by digesting copper hydroxide with a solution of the sulphate. These results were based on the analysis of the precipitates.

When an alkali is added gradually to a weak solution of copper sulphate, a point is reached when the liquid begins to show a slight alkaline reaction, but this reaction is temporary, and more alkali must be added before a permanent alkalinity is obtained. The gradual absorption of alkali after the first temporary alkalinity occurs extends over two or three days. The equivalents of alkali required to produce the initial and permanent alkaline reaction, together with the equivalents required to precipitate the copper completely, were found to be:

	Complete precipitation.	Initial alkalinity.	Permanent alkalinity.
BaO	—	0·903	0·903
CaO	0·752	0·864 0·877	0·910 0·910 0·904
Na_2O	0·766	0·833 0·851	0·904 0·897
Li_2O	—	0·808	0·903
K_2O	(0·75)	0·805	0·893
Mean	0·756	—	0·901

The precipitation of the metal is complete when the alkali reaches 0·75 equivalent, an amount showing that the basic sulphate then formed must have the formula $4CuO,SO_3$ (the value inserted for potash is that given by the investigation of 1883). This sulphate is evidently converted into a more basic one by further addition of alkali, and permanent alkalinity is reached in all five cases when the amount added amounts to 0·9 equivalent. This represents the formation of $10CuO,SO_3$. In only one instance, that of baryta, is the point of initial alkalinity identical with that of permanent alkalinity, an exception probably connected with the insolubility of barium sulphate. With lithia and potash, initial alkalinity occurs with 0·8 equivalent, but with soda and lime the values are higher. It seems most probable, however, that in all cases the point of initial alkalinity indicates the existence of a basic sulphate intermediate between the first and final products, although in some cases it may be impossible to obtain this intermediate compound unmixed with a certain amount of the final product, and hence the quantity of alkali absorbed is abnormally large. The initial alkalinity certainly marks a point at which there is a very great alteration in the rate at which the alkali disappears, an almost instantaneous absorption, changing to one of extreme slowness, although its rate varies with the alkali used. Moreover, the product obtained at the point of initial alkalinity is not intermediate in character between the highest and lowest sulphate, as it would be if it were a mixture of these two. Taking the case of lime: the first product, $4CuO,SO_3$, is a light, opaque, blue or greenish-blue substance, which settles comparatively quickly in the liquid; the final product, $10CuO,SO_3$, is of a darker, full blue colour, less opaque, and it settles much more slowly: but the intermediate product, obtained when about 0·8 equivalent is added, is almost as dark as the compound $10CuO,SO_3$, and is even more voluminous, settling very slowly indeed in the liquid. To give an example: 1 gram of hydrated copper sulphate was precipitated by different amounts of lime-water, so as to give the three basic sulphates in question, the total volume of the liquid in each case being 171 c.c.: after one hour, the precipitates occupied 83, 145 and 136 c.c. respectively, the second sulphate evidently not being intermediate in properties between the first and the third. This was repeated many times, and always with the same result.

It is fairly certain, therefore, that in the case of the action of all the alkalis (except baryta) on copper sulphate, an intermediate compound is formed, and it is probable, from the results with lithia and potash, that its formula is $5CuO,SO_3$, corresponding to the addition of 0·8 equivalent of alkali.

It is necessary to add the alkali very slowly and cautiously to the sulphate in order to obtain the first compound, $4CuO,SO_3$, pure; any local excess of alkali tends to form some of the more basic sulphates, and then, more than 0·75 equivalent will be required to complete the precipitation. In the same way, it requires great care to obtain the final sulphate, $10CuO,SO_3$, without the production of any copper hydroxide in cases where such is produced by excess of alkali, as it is where soda, lithia or potash is used, the precipitate then turning black after a time. When precipitated with care, the basic sulphates themselves seem to be quite permanent in the liquids from which they are thrown down.

It was found that the final reaction with lime-water, that is, to permanent alkalinity, was practically constant throughout the range of ordinary atmospheric temperatures, but that at higher temperatures the precipitate became less basic, attaining at 100° almost to the composition of $4CuO,SO_3$. The values obtained were:

At 5°, 0·916 CaO required. $10CuO,SO_3$ requires 0·9 CaO.
,, 25°, 0·912 ,, ,, ,, ,, ,,
,, 40°, 0·825 ,, ,,
,, 70°, 0·809 ,, ,,
,, 100°, 0·764 ,, ,, $4CuO,SO_3$ requires 0·75 CaO.

The results obtained when excess of lime-water is added to copper sulphate are described in a subsequent communication (p. 1995).

Iron Sulphates.

With ferrous sulphate, the precipitation of the whole of the iron is coincident with the first appearance of an alkaline reaction, and, although duplicate determinations were not very concordant, the complete precipitation evidently occurs when a basic sulphate of the formula $10FeO,SO_3$ is formed, analogous to the final product in the case of copper sulphate. The values obtained were:

	With Soda.	With Lime.
	0·930 equiv.	0·868 equiv.
	0·887 ,,	0·892 ,,
	0·884 ,,	0·881 ,,
	0·914 ,,	0·874 ,,
Mean	0·904 ,,	0·879 ,,

The temporary alkalinity disappears, and more alkali must be added before it becomes permanent, but the rate at which it disappears is even less than in the case of copper sulphate, and the reaction is not complete for many days. It is difficult therefore to determine the point of completion with any degree of accuracy, but it evidently corresponds with the removal of all the SO_3 from the basic sulphate; the mean of three determinations with soda gave 1·029 Na_2O as having been used, and five determinations with lime gave 1·013 CaO.

With ferric sulphate, the complete precipitation of the metal and the first appearance of alkalinity were coincident, the equivalents of alkali required being 3 × 0·772 in the case of soda, and 3 × 0·817 (mean of 0·830 and 0·803) in the case of lime. The further absorption of alkali occurs as in other cases, but with such slowness that it is almost impossible to determine the final point: using soda, this point appeared to be 3 × 0·860 equivalents. None of these values is sufficiently concordant or exact to justify the assigning of any formula to the basic sulphates formed; all that is certain is that a basic sulphate is formed, and that it is then converted by further alkali into a more highly basic one.

An investigation of the basic ferric sulphates was published by the author in 1880 (Trans., 1880, **37**, 807); the investigation was on lines different from those followed here, and, of the many basic sulphates supposed to exist, evidence in favour of one only was found, namely, $2Fe_2O_3,SO_3$; this sulphate would correspond with a reaction requiring the addition of 3 × 0·833 equivalents of alkali; the determinations just quoted give values neighbouring on this quantity, and, no doubt, this basic sulphate figures in the precipitation of ferric sulphate by alkalis.

Nickel Sulphate.

With soda, the whole of the metal was precipitated when the alkali amounted to 0·422 equivalent, and the liquid then showed a barely perceptible alkaline reaction. With lime-water, a similar result was obtained, the value found being 0·404 equivalent. This indicates the formation of $5NiO,3SO_3$. When more of either of these alkalis was added, no further increase in alkalinity occurred until the total added amounted to either 0·6 or 0·8 of an equivalent. Whether the one or the other of these two proportions marks the point at which a definite increase in the pink colour of the phenolphthalein is noticed seems to depend somewhat on the conditions under which the reaction occurs, such as the dilution of the liquid, and the rate at which the alkali is added. Both stages may sometimes be noticed in the same experiment, if the bulk of substance dealt with, and the conditions facilitating the observation of changes of colour, are suitable.

The values obtained on various occasions were:

With soda	0·598	With soda	0·812
,, lime	0·582	,, lime	0·803
,, ,,	0·596	,, ,,	0·810
Mean	0·592		0·808

These indicate the existence of $5NiO,2SO_3$ and $5NiO,SO_3$, both of which are, no doubt, formed in succession from the primary product, $5NiO,3SO_3$. The last change, to $5NiO,SO_3$, is the one which is most marked.

Cobalt Sulphate.

With cobalt sulphate, the results are different from those with nickel sulphate, for a permanent alkaline reaction appears as soon as the precipitation of the metal is complete. This occurs where the soda amounts to 0·759 equivalent, or three-quarters of that necessary for total decomposition, representing therefore the formation of $4CoO,SO_3$.

There is, apparently, a preliminary action in the case of cobalt, as in the case of the other sulphates. A faint alkaline reaction first appears when the alkali added amounts to about 0·3 equivalent, but further additions of alkali cause no corresponding increase of alkalinity until, as has been said, the amount added reaches 0·75 equivalent. This preliminary stage, however, does not serve to indicate the composition of the basic sulphate present, as part of the metal is still in solution.

The precipitate formed during this first stage is green, but when more alkali is added it becomes blue.

Manganese Sulphate.

The whole of the metal in this case was not precipitated by soda until the latter amounted to 1·019 equivalents. There is here, therefore, no indication of any basic sulphate being formed. The reaction with lime was not examined.

Zinc Sulphate.

With zinc sulphate and soda, the complete precipitation of the metal was coincident with the appearance of a permanent alkaline reaction, and no preliminary or secondary reaction was noticed. The alkali required was found to be 0·795 equivalent, indicating, therefore, the composition of the precipitate to be $5ZnO,SO_3$.

Cadmium Sulphate.

With cadmium sulphate a slight pink colour was noticed (phenolphthalein being present) on the addition of only a small amount of soda, but it is the precipitate, and not the liquid, that becomes coloured; the latter shows no alkaline reaction until the whole of the metal is precipitated. This occurs when the alkali amounts to 0·731 equivalent, indicating, although not very exactly, the formation of a sulphate of the composition $4CdO,SO_3$.

Magnesium Sulphate.

With magnesium sulphate, soda completed the precipitation when it amounted to 1·034 equivalents. No basic sulphate therefore seems to be formed in this case.

Aluminium Sulphate.

The addition of soda to aluminium sulphate completes the precipitation when the quantity added reaches 3 × 0·611 equivalents, which implies that the basic sulphate formed is $5Al_2O_3,6SO_3$. The slight excess in the soda over that calculated is accounted for by a further change, similar to that observed in other cases, since the precipitate is converted into a more basic sulphate by a further addition of alkali, the alkaline reaction not becoming permanent until the total alkali amounts to 3 × 0·95 molecules. With lime-water, a similar determination gave 3 × 0·970 molecules as requisite. The secondary action was a very slow one, requiring several days, and, possibly, was not quite complete even then, so that in all probability the final product is alumina containing no SO_3.

As many as nine basic sulphates of aluminium have been stated by various chemists to have been obtained: but an examination undertaken by the present author in 1882 (*Chem. News*, **45**, 121) threw considerable doubt on the existence of all of them as definite compounds. The list of these did not contain the one now indicated.

Summary.

Alkalis added to solutions of the metallic sulphates here examined precipitate a definite basic sulphate, except in the case of manganese and magnesium, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate, either into another, sometimes consecutively into two other, more basic products (for example, copper, nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is added in excess, the product is probably always the hydroxide, but, in the case of lime, this does not appear to be so, at any rate not with the sulphates of copper and nickel, as will be shown in the following communication. In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated by them in each particular case. The existence of the following eleven basic sulphates has been established in this way: the predominance of five as the coefficient of equivalents of metallic oxide present is very noticeable. Those marked with an asterisk are the ones formed when the whole of the metal has been precipitated from the solution, the others are products of the action of further quantities of alkali:

$5NiO,3SO_3$*, $5NiO,2SO_3$, $5Al_2O_3,3 \times 2SO_3$*, $4CuO,SO_3$*, $4CoO,SO_3$*, $4CdO,SO_3$*, $5CuO,SO_3$, $5NiO,SO_3$, $5ZnO,SO_3$*, $10CuO,SO_3$, $10FeO,SO_3$*.

The basic sulphates obtained by Habermann (*loc. cit.*), chiefly by adding ammonia to boiling solutions of the sulphates, differ in every case from the above, the compounds described by him being $7CuO,2SO_3$, $7NiO,SO_3$, $5CoO,SO_3$, $4ZnO,SO_3$, and $2CdO,SO_3$. Gorgeu also obtained $3MnO,2SO_3$, and Schindler, $2ZnO,SO_3$; the literature of the basic sulphates of copper, iron and aluminium will be found in the communications by the present author referred to above.

CXCV.—*The Chemistry of Bordeaux Mixture.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

BORDEAUX mixture, or *bouillie bordelaise*, has been in use as a fungicide since 1883. The discovery of its value was accidental. It had been the practice in the vineyards in the neighbourhood of Bordeaux to sprinkle those vines which were near a road with verdigris, in order to give them the appearance of having been poisoned, and so to prevent depredations. A mixture of lime and copper sulphate was soon substituted for the verdigris, being cheaper, and, when the downey mildew of America (*Peronospora viticola*) made its appearance in Europe, it was noticed (1882) that those vines which had received the copper dressing were those which kept their leaves longest, and were least affected by the disease.

The mixture in general use at present is made by adding 1·1 parts by weight of lime, made into a milk, to 1·6 parts of crystallised copper sulphate dissolved in 100 parts of water. This is known in America as the "normal" or "1·6" mixture. Occasionally, stronger or weaker mixtures are used, and sometimes the proportion of lime added is increased so as to be equal to that of the copper sulphate. For complete decomposition, the crystallised sulphate would require one-fifth of its weight of pure lime; therefore, the lime used in practice is always in considerable excess, even when a liberal allowance is made for impurities in it.

It is somewhat remarkable that the nature of the substance constituting this mixture has not yet been elucidated. The reaction occurring is generally represented as resulting in the formation of copper hydroxide, although occasionally it is suggested that a basic sulphate may be formed, and an equation is given representing a basic sulphate ($2CuO,SO_3$) which, so far as is known, has no existence. That copper hydroxide is the product of the reaction scarcely admits of serious consideration, for this hydroxide, as is well known, loses its water and its blue colour in a very short time, turning black, whereas Bordeaux mixture remains quite blue for an indefinite period. It is true that caustic potash in excess of that required to form basic sulphate of copper results in the formation of some copper hydroxide, and that in Bordeaux mixture the alkali is in considerable excess; but it does not by any means follow that excess of lime will behave in the same manner as excess of potash.

That the action of lime on copper sulphate is somewhat variable and complicated would appear to be probable from the considerable variations which are noticed in the blue colour of the precipitate constituting Bordeaux mixture. These variations may sometimes be explained by differences in the colour of the lime used, but they are also due, as will be seen, to the fact that there are formed, under various conditions, substances with considerable differences of coloration. Occasionally the precipitate will be found to be violet, inclining even to purple: this coloration is probably accidental, and due to the presence of some pink compound formed by organic substances exhibiting the biuret reaction. On several occasions when dealing with emulsions of petroleum with basic copper sulphate, streaks of a pink compound have been noticed in the blue emulsion.

In Bordeaux mixture made with milk of lime, there must be free lime, and, generally, calcium carbonate, mechanically mixed with the precipitate, and any direct investigation of the composition of this precipitate would be of little value. Lime-water, therefore, was used instead of milk of lime; but, even then, any analysis of the precipitate was practically impossible, for it is very bulky and difficult to wash, whilst water, as will be shown, partly decomposes it, as also does carbon dioxide. The method of examination adopted, therefore, was to mix known weights of copper sulphate and lime in solution, and to deduce the composition of the precipitate formed by determining what was left dissolved in the liquid. This is either calcium sulphate only, or calcium sulphate and hydroxide where an excess of lime has been used; the latter was determined by titration, and the former, either as barium sulphate, or by evaporation to dryness and igniting. In some cases, the precipitation was effected in the presence of excess of sodium sulphate, and then the mixed sulphates left in solution had to be discriminated by a separate determination of the amount of calcium in them.

As has been shown in the previous communication (p. 1983), the precipitation of the copper is complete when enough lime is added to form the basic sulphate $4CuO,SO_3$, and this sulphate is decomposed on further addition of alkali until the compound $10CuO,SO_3$ is formed; in addition to these, a sulphate of an intermediate composition, probably $5CuO,SO_3$, is also produced.

Although, as regards basicity, the precipitates formed when different alkalis are used are identical, a qualitative examination is sufficient to show that they are not identical in other respects. Thus, on precipitating copper sulphate with sufficient alkali to form $5CuO,SO_3$, the volume of the liquids being the same, the precipitate with lime is found to be of a pale blue, whereas that with soda is very much darker; the former, also, is either finer-grained or less dense than the latter, for, even after being allowed twenty-four hours to settle, it occupies a volume half as great again as the latter. The precipitate given by lithia resembles that with lime, and is even paler in colour and more bulky, whereas that given by potash resembles the soda precipitate, except that it is slightly darker. Similar differences in appearance are noticed if the precipitates consisting of $4CuO,SO_3$, obtained by different alkalis, are compared. The more minute state of division of the lime precipitates, as contrasted with those given by soda, is further illustrated by the greater emulsifying powers of the former, which will be described in a subsequent communication. With the basic ferrous sulphates, it may be mentioned, a like difference of behaviour characterises the precipitates thrown down by different alkalis.

These differences, however, are not of a physical character only, for the two precipitates behave differently when treated with excess of the same alkali; the soda precipitate, when treated with a further equivalent of caustic potash, begins to blacken in half an hour; with a further equivalent of soda it begins to blacken in two hours; and with an equivalent of lime, blackening commences only after about six weeks: with the lime precipitate, however, blackening is produced by excess of soda only after two or three weeks, whereas excess of neither potash nor lime seem to have any effect on it.

Passing to the quantitative examination, Table I contains the values given when copper sulphate is precipitated with varying proportions of lime. The molecular proportions of the reagents taken are entered in the first two columns, and the molecular composition of the precipitate, as given by the analysis of the residual solution, in the third. The solution of copper sulphate taken

TABLE I.—*Precipitation of Copper Sulphate by Lime-Water.*

	Proportions taken.		
	$CuSO_4$.	CaO.	Composition of precipitate.
(1)......	10	7·5	$10CuO,2\cdot5SO_3,0\cdot2\ CaSO_4$
(2)......	10	8	$10CuO,\ 2SO_3,0\cdot78CaSO_4$
(3)......	10	8	$10CuO,\ 2SO_3,0\cdot46CaSO_4$
(4)......	10	9	$10CuO,\ SO_3,1\cdot45CaSO_4$
(5)......	10	9	$10CuO,\ SO_3,1\cdot34CaSO_4$
(6)......	10	9	$10CuO,\ SO_3,1\cdot25CaSO_4$
(7)......	10	18	$10CuO,SO_3,1\cdot12CaSO_4,2\cdot66CaO$
(8)......	10	18	$10CuO,SO_3,0\cdot88CaSO_4,3\cdot00CaO$
(9)......	10	27	$10CuO,SO_3,1\cdot11CaSO_4,3\cdot05CaO$
(10)......	10	27	$10CuO,SO_3,1\cdot11CaSO_4,2\cdot73CaO$
(11)......	10	36	$10CuO,SO_3,0\cdot84CaSO_4,3\cdot11CaO$
		Mean	$10CuO,SO_3,1\cdot01CaSO_4,2\cdot91CaO$
(12)......	10	54	$10CuO,SO_3,1\cdot38CaSO_4,4\cdot44CaO$
(13)......	10	108	$10CuO,SO_3,0\cdot98CaSO_4,7\cdot24CaO$
(14)......	10	180	$10CuO,0\cdot47SO_3\quad 15\cdot7CaO$
(15)......	10	240	$10CuO,\quad 18\cdot6CaO$
(16)......	10	300	$10CuO,\quad 20\cdot6CaO$
(17)......	10	490	$10CuO,\quad 28\cdot1CaO$
(18)......	10	1020	$10CuO,\quad 32\cdot6CaO$
(19)......	10	1840	$10CuO,\quad 28\cdot5CaO$
(20)......	10	5100	$10CuO,\quad 31\cdot4CaO$
		Mean	$10CuO,\quad 30\cdot1CaO$

contained 10 per cent. of $CuSO_4,5H_2O$, and the lime-water contained about 0·135 per cent. of CaO; in the case where the smallest proportion of lime-water was used, the mixture would be of about half the strength of normal Bordeaux mixture. The proportions in the table are all expressed so as to refer to 10CuO.

In the first six experiments, the lime added was only just sufficient to form one or other of the three definite basic sulphates, but in all three cases, as will be seen, these contain a certain amount of calcium sulphate. With $4CuO,SO_3$ (No. 1), the amount is very small, with $5CuO,SO_3$ (Nos. 2 and 3) it is much greater (although it varies considerably in the duplicate determinations), and with $10CuO,SO_3$ (Nos. 4–6) it is greater still, there being then more SO_3 present as calcium sulphate than in the basic copper sulphate itself. Taking into consideration the large and approximately constant proportion of calcium sulphate in the latter case, and the fact that the amount here present is very different from what it is with the less basic sulphates, the conclusion is that the calcium sulphate must be present as a chemical constituent of the molecule itself. The values, however, are not sufficiently near to a simple proportion to lead to a definite formula for the complex sulphate.

No doubt, all these precipitates are unstable compounds, the composition of which would be affected by such circumstances as the temperature and strength of the solution; indeed, they readily give up some of their calcium sulphate to water. This was established as follows: the mixture in No. 6 was filtered, and the filtrate measured and analysed; the measurement showed what volume of liquid was retained by the precipitate on the filter; the precipitate with this liquid was then mixed with water equal in volume to that originally present, and the amount of sulphate passing into solution was determined. This was found to be greater than that in the liquid adhering to the precipitate, so that some of the sulphate must have been derived from the precipitate itself. The precipitate, which originally contained $1·25CaSO_4$, contained now only $1·01CaSO_4$. A similar experiment with the less basic precipitate in No. 3 gave similar results, the $0·46CaSO_4$ originally present being reduced to $0·35CaSO_4$.

The circumstances conditioning the amount of calcium sulphate in these basic sulphates were examined in other experiments, which may be described before dealing with the further results given in Table I.

Table II contains results in which the precipitation was effected in the presence of excess of calcium sulphate. In Nos. 23, 21, 26, 27 and 24 the calcium sulphate added was equivalent to one, two,

TABLE II.—*Precipitation of Copper Sulphate by Lime-Water with Excess of Calcium Sulphate Present.*

	Proportions taken.			
	$CuSO_4$.	CaO.	$CaSO_4$.	Composition of precipitate.
		(*a*). $4CuO,SO_3$ formed.		
(1)	10	7·5	0	$10CuO,2·5SO_3,0·2CaSO_4$
(21)	10	7·5	15	$10CuO,2·5SO_3$, (no $CaSO_4$)
(22)	10	7·5	Saturated	$10CuO,2·5SO_3,0·27CaSO_4$
		(*b*). $5CuO,SO_3$ formed.		
(2) (3)	10	8	0	$10CuO,2SO_3,0·62CaSO_4$
(23)	10	8	8	$10CuO,2SO_3,0·14CaSO_4$
(24)	10	8	24	$10CuO,2SO_3,0·20CaSO_4$
(25)	10	8	Saturated	$10CuO,2SO_3,0·78CaSO_4$
		(*c*). $10CuO,SO_3$ formed.		
(4) (5) (6)	10	9	0	$10CuO,SO_3,1·35CaSO_4$
(26)	10	9	18	$10CuO,SO_3,1·43CaSO_4$
(27)	10	9	18	$10CuO,SO_3,1·03CaSO_4$
(28)	10	9	Saturated	$10CuO,SO_3,1·15CaSO_4$

two, two and three times respectively, that formed in the reaction, excess of lime-water neutralised with sulphuric acid being added for the purpose; but the water present was increased in similar proportion, so that the strength of the solution as regards its calcium sulphate contents was the same in all cases. All these solutions, however, were supersaturated with calcium sulphate, for 100 parts of water at 15° dissolve 0·129 gram of lime, but only 0·197 gram of calcium sulphate (equivalent to 0·081 gram CaO), so that the amount available for combining with the basic sulphate would be increased by increasing the amount of calcium sulphate solution present, yet no such increase of sulphate in the precipitate is produced thereby.

The supersaturated solution of calcium sulphate obtained by neutralising lime-water with sulphuric acid remains very persistently supersaturated, and no trace of sulphate is deposited for at least forty-eight hours; it is improbable therefore that these precipitates were contaminated with calcium sulphate which had crystallised out, as they were all filtered from the liquid within twenty-four hours of being precipitated. To obviate such a possibility, however, the experiments were repeated in the presence of a large weighed crystal of selenite, on to which any calcium sulphate would be deposited from the liquid, whilst, at the same time, the liquid would be kept saturated. The mixtures were left for nine weeks before analysis (which included the determination of the increase in weight of the selenite crystals); the results (Nos. 22, 25 and 28) give substantially the same values as the other experiments for the composition of the precipitates. It should be mentioned, however, that one series made at a lower temperature gave higher values in the case of all three basic sulphates for the amount of calcium sulphate present; this series has not been included here, as there was another circumstance connected with it which prevented its being strictly comparable with the others.

Of the three basic sulphates, $10CuO,SO_3$ is the one in which the calcium sulphate contents show least variation. The mean of the various determinations gives the approximate formula for this compound as $10CuO,SO_3,1·28CaSO_4$; the means for the other basic sulphates are $10CuO,2SO_3,0·47CaSO_4$ and $10CuO,2·5SO_3,0·16CaSO_4$.

For reasons connected with an investigation which will be described later, it was necessary to ascertain whether the composition of these basic copper sulphates was modified by the presence of excess of sodium sulphate in the solution. With this object in view, known quantities of sodium sulphate were added to the copper sulphate before the addition of the lime. The results are given in Table III. With the basic sulphate $4CuO,SO_3$, the small amount of calcium sulphate present in it is entirely ousted, and its place

TABLE III.—*Precipitation of Copper Sulphate by Lime-Water with Sodium Sulphate Present.*

	Proportions taken.			
	$CuSO_4$.	CaO.	Na_2SO_4.	Composition of precipitate.
		(*a*).	$4CuO,SO_3$ formed.	
(1)…………	10	7·5	0	$10CuO,2·5\ SO_3,0·2\ CaSO_4$
(29)…………	10	7·5	30	$10CuO,2·55SO_3,0·75Na_2SO_4$
		(*b*).	$5CuO,SO_3$ formed.	
(2) (3) ……	10	8	0	$10CuO,\quad 2SO_3,0·62CaSO_3$
(30)…………	10	8	30	$10CuO,2·02SO_3,0·34CaSO_4,0·83Na_2SO_4$
		(*c*).	$10CuO,SO_3$ formed.	
4) (5) (6)…	10	9	0	$10CuO,\quad SO_3,1·35CaSO_4$
(31)…………	10	9	15	$10CuO,1·05SO_3,1·03CaSO_4,0·9\ Na_2SO_4$
(32)…………	10	9	30	$10CuO,1·09SO_3,1·21CaSO_4,0·82Na_2SO_4$
(33)…………	10	9	45	$10CuO,1·01SO_3,0·99CaSO_4,1·41Na_2SO_4$
(34)…………	10	9	45	$10CuO,1·02SO_3,0·77CaSO_4,1·27Na_2SO_4$
	Mean of 24 to 27 ………			$10CuO,1·04SO_3,1·00CaSO_4,1·10Na_2SO_4$

is taken by a proportionately large amount of sodium sulphate. A similar change occurs with both the other basic sulphates, although the displacement of the calcium sulphate is not complete; with $5CuO,SO_3$ about half the calcium sulphate is removed, and with $10CuO,SO_3$ about two-thirds; whilst in all cases the amount of sodium sulphate in the precipitate is greater than that of the calcium sulphate which it displaces.

The four determinations with the most basic sulphate clearly indicate a definiteness in composition, for the sum of molecular proportions of sodium and calcium sulphates present is constant, in spite of the variations in the proportions of sodium sulphate taken, and the precipitate is representable by the formula

$$10CuO,SO_3,2(Na_2,Ca)SO_4.$$

In only one of the determinations (33) are the values at all at variance with this formula, but the experimental errors are considerable, for the amount of SO_3 in the precipitate is determined from the difference between quantities of ten to twenty times its magnitude, and the lime to be determined is present in very small amount. It is probable, indeed, that the molecular proportions of calcium and sodium sulphate are constant throughout, instead of being merely interchangeable, and the mean of the results, as will be seen, gives almost exactly equal molecular proportions of these two.

It will be noticed that the SO_3 united with the copper oxide is not, in these cases, represented by an exact number of equivalents; this is because the values given are dependent on the analysis, being the difference between the total SO_3 in the precipitate and that united with the lime and soda present, instead of being deduced, as in other cases, from the amount of lime-water neutralised.

With the two less basic sulphates, the experiments were not extended so as to determine the exact formula of the precipitates; it is noticeable, however, that with the second sulphate the formula approximates to $10CuO,2SO_3,(Na_2,Ca)SO_4$, that is, a compound containing only half as much of the neutral sulphates as is present in the most basic sulphate. In all three cases the proportion of total SO_3 to CuO in the molecule seems to be nearly constant, and approximates 3 : 10; the less there is present in combination with the copper the more there is present as sulphate of calcium or sodium.

Reverting now to Table I, the experiments in the lower portion of it refer to cases where lime is added in excess. The results are somewhat remarkable. With all proportions of lime between 10 and 40 CaO to each 10CuO (Nos. 7 to 11) the same compound is formed, this being the basic copper sulphate combined with one molecule of calcium sulphate and three of calcium oxide, or, in other words, a double basic sulphate of copper and calcium of the formula $10CuO,SO_3,4CaO,SO_3$. When the proportion of lime taken is increased beyond 40CaO to each 10CuO, the precipitate rapidly becomes more basic, and with proportions exceeding 100CaO the SO_3 in it begins to disappear, until, with still greater excess of lime, we get a precipitate which is a double oxide of copper and calcium. This attains to a constant composition when the proportion of lime reaches about 500CaO to 10CuO, and remains so up to the end of the series, where 5100CaO to 10CuO was taken. The composition of this double oxide is CuO,3CaO; the mean of the last four determinations giving CuO,3·01CaO.

Between the double oxide and the double basic sulphate

$$10CuO,SO_3,4CaO,SO_3,$$

there is probably another definite compound formed, and, as the lower basic sulphates of calcium and of copper appear to be analogous ($4M''O,SO_3$), we may conjecture that the higher ones are so also, and that the highest double basic sulphate has the formula $10CuO,SO_3,10CaO,SO_3$. The values found in No. 13 are very close to this, being $10CuO,SO_3,8{\cdot}2CaO,SO_3$, but it would require several determinations with amounts of lime intermediate between those in Nos. 13 and 14 to settle whether the limit here suggested is really reached before the SO_3 begins to be abstracted from the molecule.

The existence of this second double basic sulphate is emphasised when the results are plotted out. Plotting the lime in the precipitate against the amount of lime taken (it is best to take the logarithms of these quantities), it is clear that the values, when the precipitates contain $CaSO_4$, are not continuous with those when they contain none; the experiments 11 to 13 lie on one straight line, and 14 to 17 on another, there being some considerable change between 13 and 14. The rest of the figure is made up of three horizontal lines, the first representing the results of Nos. 1 to 6, where there is no lime in the precipitate, and the second representing the results of Nos. 7 to 11, where the double basic sulphate is formed, and the third, the results of Nos. 17 to 20, when the double oxide has attained constancy of composition.

In Bordeaux mixture, the highest proportion of lime generally used is five equivalents to each equivalent of copper sulphate, that is, equal weights of the two; this is about the proportion in experiment 12 in Table I, but, as the lime is always far from pure, the actual proportions of calcium oxide would be smaller, and the reaction occurring would rarely go beyond the stage reached in experiments 7 to 11, that is, $10CuO,SO_3,4CaO,SO_3$ would be the com-compound formed. With still smaller proportions of lime, or with impure and carbonated lime, we should get the compound

$$10CuO,SO_3,1{\cdot}3CaSO_4,$$

or even a less basic sulphate down to $4CuO,SO_3$. The different appearance of these products would account for the differences observed in the appearance of Bordeaux mixture, the basic sulphates, $4CuO,SO_4$ and $10CuO,SO_3,4CaO,SO_3$, being much paler in colour than the intermediate sulphates.

When Bordeaux mixture is applied to trees, it liberates, after a time, small quantities of copper sulphate, and it is to this soluble copper that its fungicidal action is attributable. The reaction, no doubt, consists of $xCuO,ySO_3 + (x-y)CO_2 = (x-y)CuCO_3 + yCuSO_4$.

One of the disadvantages attending its use, however, is that a certain time elapses before the fungicidal action comes into play. The nature of the compound of which Bordeaux mixture has now been found to consist, will explain the occurrence of this delay, for, with a basic sulphate of copper and calcium, the basic sulphate of copper would probably not be attacked by the carbon dioxide until all the basic sulphate of calcium in it had been decomposed. That this is the case was verified by suspending in equal bulks of water various basic sulphates containing the same amount of copper, passing the same slow stream of carbon dioxide through the liquids, and testing these at intervals to ascertain how long it took before recognisable quantities of copper passed into solution. The results were as follows:—

With $10CuO,2{\cdot}5SO_3,0{\cdot}16CaSO_4$	3—5 minutes
,, $10CuO,2SO_3,0{\cdot}47CaSO_4$	10 ,,
,, $10CuO,SO_3,1{\cdot}28CaSO_4$	10 ,,
,, $10CuO,SO_3,4CaO,SO_3$	45 ,,

The length of the interval in the case of the last compound, as compared with that in the case of the others, is very noticeable. Excess of lime had, of course, to be added to precipitate the last sulphate, but that was removed by filtration before the precipitate was treated with the carbon dioxide; when it was not removed (and this is the case with Bordeaux mixture in practice) a still longer interval, namely, seventy-five minutes, elapsed before copper was liberated. The longer interval in the case of the second and third sulphate, as compared with the first, is, of course, due to the smaller amounts of copper sulphate which they are able to liberate.

The delay in the action of the fungicide would, therefore, be obviated by using only sufficient lime to produce the basic sulphate $4CuO,SO_3$, instead of the double basic sulphate $10CuO,SO_3,4CaO,SO_3$; there would also be a considerable economical advantage in doing so, for the fungicidal value depends on the amount of normal copper sulphate eventually liberated, and the basic sulphate $4CuO,SO_3$ will liberate two and a half times as much of the normal sulphate as will $10CuO,SO_3$, calculated on the same weights of copper sulphate used in preparing them. If, on the other hand, the proportion of lime used were increased to about five times that of the copper sulphate (actual weights), the insecticidal value would be entirely destroyed, for the product then would consist of the double oxide, without any SO_3 in it.

To make the basic sulphate $4CuO,SO_3$, it is necessary to use lime-water instead of milk of lime, and this would be a further advantage from several other points of view, for the presence of solid lime clogs and wears the spraying nozzles, and entails loss of material, owing to its being easily knocked off the leaves.

One part by weight of crystallised copper sulphate requires about 134 c.c. of lime-water for its precipitation (the completion of which should, of course, always be verified by testing with ferrocyanide);* any increase in the proportion of lime would result in a diminution of the fungicidal value; thus, an increase to 143 c.c. would result in the precipitation of $10CuO,2SO_3,xCaSO_4$, and a consequent reduction of the efficacy by one-fifth.

A Bordeaux mixture made as here suggested would be rather more efficacious than the "normal" mixture, although it would contain less than half the amount of copper, and would also cost less than half. Of course, the volume of lime-water required would vary somewhat with the temperature, but the variation in solubility of lime throughout the range of ordinary atmospheric temperatures is small, being given as 0·137 part in 100 parts of water at 5°, and 0·125 part at 20°. According to these values, 135 c.c. would be required at 5°, and 123 c.c. at 20°, to precipitate the copper in one gram of $CuSO_4,5H_2O$. The former agrees almost exactly with the amount (134 c.c.) which has been found necessary in practice when working either at winter or summer temperatures.

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* A solution containing 0·002 per cent. of $CuSO_4,5H_2O$ gives a visible coloration with ferrocyanide.

A few experiments were made using caustic soda (free from carbonate) instead of lime-water. The results are given in Table IV.

TABLE IV.—*Precipitation of Copper Sulphate by Caustic Soda.*

	Proportions taken.			
	$CuSO_4$.	Na_2O.	Na_2SO_4.	Composition of precipitate.
(35)	10	7·5	—	$10CuO, 2{\cdot}5SO_3, (0{\cdot}01Na_2SO_4)$
(36)	10	8	—	$10CuO, 2SO_3$, (no Na_2SO_4)
(37)	10	9	—	$10CuO, SO_3, 0{\cdot}06Na_2SO_4$
(38)	10	9	15	$10CuO, SO_3, 0{\cdot}5\ Na_2SO_4$
(39)	10	9	45	$10CuO, SO_3, 1{\cdot}33Na_2SO_4$

When the basic sulphates formed are $4CuO,SO_3$, or $5CuO,SO_3$, there is no sodium sulphate combined with them, and where $10CuO,SO_3$ is the product, the amount is so small that it is almost within the limits of experimental error, namely, $0{\cdot}06Na_2SO_4$. When an excess of sodium sulphate is present, however, the amount in the precipitate is increased, but the experiments were not extended far enough to show what ultimate limits are attained. The absence of any sodium sulphate in the precipitate consisting of the less basic sulphates is in harmony with a similar observation made in 1883 (*Chem. News*, **47**, 182) as regards $4CuO,SO_3$ when precipitated by potash.

The differences in the appearance and behaviour of the basic sulphates of copper when they are precipitated by lime or soda is fully explained by these results (see p. 1990), for identical substances are not formed in the two cases, although the proportions of $CuO:SO_3$ are the same.

The behaviour of different alkalis towards other metallic sulphates indicates differences similar to those observed in the case of copper sulphate. This is evidently so with ferrous sulphate, the precipitate formed by lime being different in colour and much more bulky, when compared with that formed by soda, although with both alkalis the basicity is the same, $10M''O,SO_3$ (p. 1984). Ferrous sulphate, however, is not a convenient salt for investigation, owing to its absorption of oxygen, and a few experiments were made with nickel sulphate instead.

TABLE V.—*Precipitation of Nickel Sulphate by Lime-Water.*

	Proportions taken.			
	$NiSO_4$.	CaO.	Na_2SO_4.	Composition of precipitate.
(40)	10	8	—	$10NiO, \quad 2SO_3,0·11CaSO_4$
(41)	10	24	—	$10NiO,0·34SO_3,2·48CaO$
(42)	10	48	—	$10NiO,0·49SO_3,3·64CaO$
(40)	10	8	0	$10NiO, \quad 2SO_3,0·11CuSO_4$
(43)	10	8	17	$10NiO,1·74SO_3,0·16CaSO_4$
(44)	10	8	52	$10NiO,1·91SO_3,0·64CaSO_4$

The results are given in Table V. The most basic sulphate of nickel had been found to be $5NiO,SO_3$ (see p. 1985), and this sulphate alone was examined. As seen from No. 40, it, like the corresponding copper compound (Nos. 2 and 3, Table I), contains some calcium sulphate, but in quantity so small that it might almost be attributed to experimental error. On raising the amount of lime used beyond that required for the formation of the basic sulphate, we get, unlike the case of copper, an immediate and considerable reduction in the SO_3 present, the composition of the precipitate being substantially that of a double oxide of nickel and calcium, a small amount only of calcium sulphate being present. Thus, in the two cases, we get $10NiO,2CaO,0·4CaSO_4$ and

$$10NiO,3CaO,0·6CaSO_4.$$

Whether the calcium sulphate would be entirely eliminated or not by a further increase in the amount of lime was not determined.

When the basic sulphate is precipitated in the presence of excess of sodium sulphate (Nos. 43 and 44), no sodium sulphate enters into its composition as it does in the analogous case with copper (Table III), but the proportion of calcium sulphate in it is increased instead, the partial saturation of the liquid by the sodium sulphate having, apparently, facilitated the abstraction of calcium sulphate from it. Clearly the tendency of basic nickel sulphate to combine with neutral sulphates is feeble as compared with that of basic copper sulphate.

It will be seen that in Nos. 43 and 44 the analytical numbers indicate that some of the SO_3 has been abstracted from the basic sulphate. The mixtures were left standing for several days after a portion of the liquid had been withdrawn for analysis, and it was found that the remaining liquid gradually assumed a green colour, the nickel passing slowly into solution again; doubtless some soluble double sulphate of nickel and sodium was being formed. The formation of a certain amount of such a compound before the liquid had been withdrawn for analysis would account for the deficiency of SO_3 in the precipitate.

The examination of nickel sulphate having shown that it was not suitable for an investigation which was in contemplation, the subject was not pursued. The results, however, are sufficient to prove that, whilst the basic sulphates of different metals exhibit certain points of similarity in their behaviour towards excess of alkali and of neutral sulphates, each metal shows peculiarities of its own, and the actual products could only be determined by a separate examination in each case.

Summary.

The substances formed on the addition of lime to copper sulphate, as in the preparation of Bordeaux mixture, are dependent on the proportions of lime used, and may be either (approximately so far as the $CaSO_4$ is concerned):

(1) $4CuO,SO_3,0{\cdot}06CaSO_4$,
(2) $5CuO,SO_3,0{\cdot}25CaSO_4$,
(3) $10CuO,SO_3,1{\cdot}3CaSO_4$,
(4) $10CuO,SO_3,4CaO,SO_3$,

(possibly 5) $10CuO,SO_3,10CaO,SO_3$, or (6) $CuO,3CaO$; that present in most cases probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having to be decomposed before the basic copper sulphate is attacked. By using only sufficient lime to form $4CuO,SO_3$, the presence of basic calcium sulphate, and the consequent delay in the action, is avoided; in addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken), and the insecticidal value of the mixture, will be two and a half times as great as when it consists of $10CuO,SO_3,4CaO,SO_3$.

To obtain the basic sulphate $4CuO,SO_3$, one gram of crystallised copper sulphate in solution must be precipitated by adding about 134 c.c. of lime-water. This mixture is rather more effective than the "normal" Bordeaux mixture, made with more than double the amount of copper sulphate precipitated by milk of lime in excess.

When copper sulphate is precipitated by lime in presence of excess of sodium sulphate, the precipitate contains sodium sulphate, as well as calcium sulphate; with the most basic sulphate, its formula is $10CuO,SO_4,2(Na_2,Ca)SO_4$, or $10CuO,SO_3,Na_2SO_4,CaSO_4$.

The basic sulphates of copper precipitated by soda contain no appreciable amount of sodium sulphate, unless a large excess of sodium sulphate is present in the liquid. They therefore differ essentially from those obtained with lime, although the basicity is the same in the two cases.

Nickel sulphate with lime gives a basic sulphate containing a very little calcium sulphate, but if the lime is at all in excess, the basic sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide of nickel and calcium. If excess of sodium sulphate is present in the liquid, the precipitate contains more calcium sulphate, but the results are complicated by some of the nickel redissolving to form (probably) a double sulphate of nickel and sodium.

CXCVI.—*Emulsions.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Emulsions with Soluble Emulsifiers.

When any liquid insoluble in water is mixed with the latter and broken up into minute globules, as when it is forced through a syringe, the globules remain more or less permanently emulsified whenever the water contains soap or some other emulsifying agent in solution. The whole of the liquid, however, is not an emulsion, properly so called, but a mixture of the emulsion with excess of soap solution; on standing, the true emulsion separates, and, if the substance emulsified is lighter than water, rises to the surface. This is precisely analogous to the separation of cream from milk.

The time required for an emulsion to rise, and for the volume occupied by it to become constant, depends, naturally, on various circumstances, and varies between several days and many weeks. The line of demarcation between the emulsion and the excess of liquid is generally well marked, for the liquid becomes almost clear, and, if it contains much soap, quite clear, whilst the emulsion is opaque. In many cases, the emulsion itself separates into two layers, evidently of different composition, the line of demarcation between these being fairly distinct.

A rise of temperature facilitates emulsification with soap solutions, but there appears to be no difference between emulsions of the same composition when made at different temperatures. For each temperature, and for each proportion of paraffin oil, the quantity of emulsifier which must be present ranges between certain definite limits; thus, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain from about 0·7 to 1·8 per cent. of potash soap; but for 40 volumes of oil to 60 of water, emulsification is possible with from 0·3 to over 25 per cent. of soap. The explanation of the existence of such limits (especially of the superior limit) will be discussed below, but it may be remarked that the above figures apply to only one particular soap, and that soaps, even when of the same brand, vary greatly in their emulsifying power, it being difficult to obtain emulsification at all in some cases, even with the aid of heat.

Emulsification appears to occur suddenly: when soap is used, and the solution is not very strong, it is possible to judge immediately by the working of the syringe whether it has occurred or not; but when it has not occurred, no continuance of the pumping, without altering other conditions, will produce emulsification.

The increase of viscosity on emulsification is easily explained by the great increase in the extent of the oil-water surface on the oil being reduced to minute globules. An ordinary emulsion, although containing 70 to 80 per cent. of mobile paraffin oil, is as viscid as thick cream, and its viscidity increases with the proportion of oil present, even when that oil is a very light one, such as a benzine. With very high percentages of oil, the emulsion becomes practically solid, resembling a blancmange. Emulsions containing as much as 99 per cent. of ordinary lighting oil have been made, the remaining 1 per cent. being a 1 per cent. solution of soap. Such strong emulsions, however, cannot be obtained directly; they must be made by taking a weaker emulsion, and gradually increasing the paraffin in it, churning it after each addition. Even these strongest emulsions are true emulsions of the oil; that is, it is the oil which is in globules, and the water, although so small in amount, which is the menstruum. There are no signs of the existence of an emulsion of water in oil. As a consequence of this, an emulsion (even a 99 per cent. one) will mix perfectly with water to form a weaker emulsion, but it will not mix with more paraffin, unless, of course, that paraffin is emulsified with it by further churning. Indeed, the addition of any paraffin in bulk to an emulsion eventually causes the de-emulsification of the whole, the globules of the emulsion being attracted by, and coalescing with, the mass of unemulsified paraffin. It is for this reason that an imperfectly made emulsion will eventually de-emulsify on standing, and so will a very strong emulsion, for it is generally an imperfect emulsion also, as it is so viscid that the whole of the paraffin in it cannot be churned up with it properly. Spontaneous de-emulsification is usually a question of weeks or months, sometimes of years; possibly a very perfect emulsion would never de-emulsify spontaneously at all, but once de-emulsification has started, it progresses at an increasing rate.

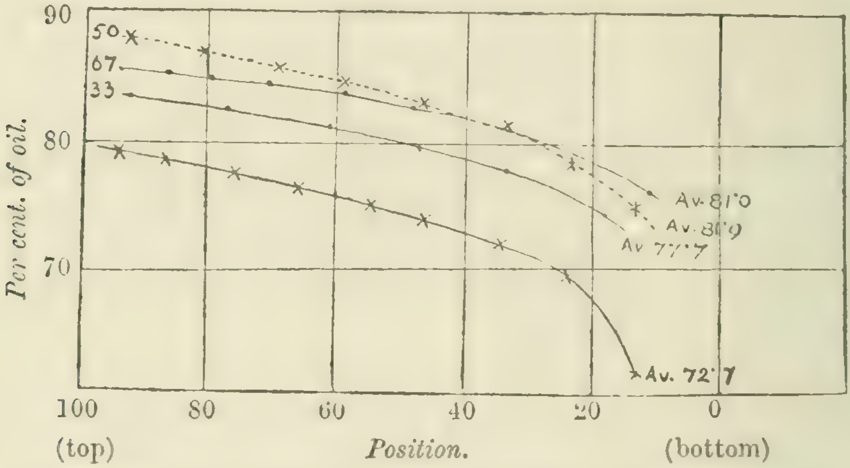
Strong emulsions, especially the semi-solid ones, are very bad conductors of heat. When one of them is heated in a wide test tube, it partially melts, de-emulsifies, and boils; but, although the boiling point may be 160° to 170°, ebullition can be continued for five or ten minutes, while a nucleus of the emulsion remains at a temperature far below 100° in the centre of the boiling paraffin. The water becomes gradually concentrated in this nucleus, and finally volatilises explosively.

Although one of these semi-solid emulsions, when kept in a closed vessel, will only gradually de-emulsify in the course of months, yet, when exposed to dry air, it will do so in a very short time; the edges of the lumps assume the appearance of a transparent, slightly blue jelly, and the whole liquefies in the course of some hours. No such change occurs in moist air. It is evident, therefore, that the change to the transparent condition must be due to the loss of moisture, but it is difficult to see in what the change consists. The opaque emulsion appears to contain a few globules of about 0·0003 mm. in diameter, but the bulk of it seems to be devoid of structure, and, if composed of globules, as presumably it is, these must be less than 0·0001 mm. in diameter. The transparent jelly presents nothing at all visible under the microscope. Thus the difference between them seems to consist in the presence or absence of a few larger globules, but why these should disappear throughout the mass on exposure to air is not at all clear. The transparent jelly is as stable as the opaque emulsion, when kept in a closed vessel. On placing a portion of it in water it instantly becomes opaque, and gradually disseminates in the water, forming a weak, milky emulsion.

In a collection of close-packed spheres of uniform size, whatever that size may be, the volume of the spheres is 74·048 per cent. of the total volume of the mass; with an emulsion of uniform spheres, the volume of the oil would be less than this, as the spheres are not in actual contact, the separating film of medium being of appreciable thickness. But in emulsions, the spheres are not uniform, and there does not therefore appear to be any reason why the ratio of the volume of the oil to the total volume of emulsion should be of any particular magnitude. The ratios actually found, however, do not differ very widely from that for close-packed uniform spheres, being generally from 65 to 82 for every 100 volumes of emulsion. This is independent of the proportions in which the oil and solution are taken to start with, so long as the former does not exceed 80 per cent.

In a number of experiments which were quoted in the Woburn Report, the proportions for the oil to water composing emulsions were found to be in the simple ratios of 2 : 1, 3 : 1, or 4 : 1. It was not possible to suggest any explanation of this, and the results (although similar ones have been obtained subsequently) were probably fortuitous. This seems to be established by the fact that these emulsions vary more or less in composition throughout their mass. The nature of this variation will be seen best by an inspection of Fig. 1. Three emulsions were made by churning a 1 per cent. soap solution with "Solar Distillate," a paraffin oil distilling almost entirely between 240° and 350°, sufficient to make mixtures containing, respectively, 67, 50 and 33 per cent. by volume of the oil. These were left undisturbed for twelve weeks, after which the emulsions, which had risen to the top, contained, on the average, 81·0, 81·9 and 77·7 per cent. of oil, in the three cases, respectively. The emulsions were

FIG. 1.



Composition of emulsions. "Solar Distillate" in soap solutions.

analysed from top to bottom, removing for the purpose successive layers, and analysing each by adding to it a trace of acid, which de-emulsified it. The percentage (by volume) of oil diminishes throughout from the top of the column downwards, but very slowly at first, and more rapidly towards the bottom. The examination cannot well be extended to the very bottom of the column, as it is difficult to remove the emulsion without drawing with it some of the watery liquid from below. The three emulsions, as will be seen, do not differ much in composition, in spite of the different proportions of the oil and solution taken in their manufacture, and such differences as exist do not vary regularly with these proportions. In none of these cases were there visible any different zones, such as are often noticed, but the analysis gives some evidence of the existence of one in the case of the curve marked 67, for the first three portions removed, embracing a quarter of the whole emulsion, gave the same values, namely, 84·7, 84·5 and 84·6 per cent. A more conspicuous instance of the arrangement in zones of equal strength will be mentioned below.

The emulsification of 50 per cent. of paraffin was repeated with a 5 per cent., and with a 0·2 per cent. solution of soap as well. The results with the former, when plotted, were almost coincident with those with the 1 per cent. solution shown in the figure (marked 50); those with the 0·2 per cent. solution gave lower values throughout, and are represented by the lowest curve in the diagram.

Differences, such as those exhibited between the emulsions portrayed in Fig. 1, are, no doubt, merely due to differences in the size of the globules, and must be largely accidental. An examination under the microscope was sufficient to indicate that the average size of the globules in the emulsion giving the lowest curve was somewhat greater than that in the others, although no differentiation of these others amongst themselves was possible.

All emulsions contain globules of different sizes, and it is possible to form only a very rough estimate as to what is the average, or, rather, most frequent, size of the globules present. With most paraffin oils emulsified in soap solutions containing from 5 to 0·5 per cent. of soap, the most frequent size seems to be about 0·0075 mm. in diameter, but there are present some globules of three or four times this size, as well as smaller ones down to one-tenth of it, or less. In the semi-solid emulsions, as already stated, the globules are much smaller. Imperfect churning of the mixture results in larger globules, but a dozen vigorous strokes of a syringe fitted with a rose jet seems to be sufficient to break up the oil as far as is possible. A deficiency in the proportion of soap to the paraffin results in larger globules, and, if reduced too far, no permanent emulsification can be obtained.

The character of the oil, also, has an effect on the size of the globules; emulsions with the lighter paraffins, such as the various benzines and motor spirits (sp. gr. 0·7 to 0·75), are more coarse-grained than those with lighting oils (sp. gr. 0·8) or "Solar Distillates" (sp. gr. 0·86); but with mineral naphtha and benzene, the reverse is the case, emulsions with these being exceptionally fine-grained. With crude petroleum, sp. gr. 0·955 (which contains much vaseline), a very thick, unmanageable emulsion is obtained. Turpentine and olive oil do not emulsify with soap solution in the same way as do the paraffin oils, a large portion of the material remains unemulsified, and the line of demarcation between the layers of different composition is not clearly marked. With turpentine, that portion of the mixture which most resembles an emulsion contains only 5 to 6 per cent. of the oil, but with olive oil there is a small layer, intermediate between the free oil on the top and the solution at the bottom, which appears to be a true emulsion, as it contains about 70 per cent. of oil.

Compared with the oil globules in cream, paraffin emulsions are more coarse-grained, and much less uniform. In cream, the globules are 0·003 to 0·005 mm. in diameter. They are, however, collected together in groups, and are not distributed uniformly throughout the medium as in the case of paraffin emulsions.

So long as thorough emulsification has been produced, there does not appear to be marked variations in the size of the globules of an emulsion throughout the mass; the only difference observable between the upper and lower layers is, that in the former the globules are more closely packed than in the latter.

Other soluble substances, besides soap, will act as emulsifiers for paraffin, and some of them are used practically in America. Sour milk and scorched flour are amongst the latter, and the author has also examined the results obtained with solutions of glue, starch, egg-albumen, saponin and extract of quillaia bark. All these substances give emulsions more or less closely resembling those with soap, but they all appear to be inferior to the latter as regards the fineness of texture of the product, and, consequently, the emulsions separate from the excess of liquid more rapidly. With saponin and quillaia, this is notably so, and with proportions of these materials which have been recommended for use (0·025 per cent. of quillaia), emulsification is so unsatisfactory that de-emulsification sets in after twenty-four hours, whilst, if the proportion of paraffin taken for the mixture is large (67 per cent.), only partial emulsification is obtainable. With some of the other substances mentioned above, for example, milk, it is not possible to obtain a strong emulsion unless the paraffin is added gradually, churning after each addition.

De-emulsification.

The de-emulsification of an emulsion may be brought about, (1) by the presence of unemulsified paraffin, as already mentioned; (2) by adding a liquid, such as alcohol, in which the paraffin and water are both soluble; or (3) by destroying the emulsifier. The most convenient de-emulsifier to use when determining the percentage of oil in an emulsion made with soap is a small quantity of mineral acid. With a very strong semi-solid emulsion, a mere trace of hydrochloric acid is sufficient to convert it almost instantly into a mass of liquid oil, with a few drops of water below it. Any sodium salt produces de-emulsification, owing to the conversion of the potassium soap into the comparatively insoluble sodium soap. De-emulsifying action does not appear to be in any way dependent on the de-emulsifying agent being an electrolyte, for potassium salts are without effect on emulsions in potassium soap, and even hydrochloric acid will not produce de-emulsification (as will be shown immediately) in cases where the emulsifying agent is not destroyed by it.

In the Woburn Report, it was shown that a paraffin emulsion containing 2 per cent. of caustic soda possessed valuable insecticidal and detergent properties, but the practical de-emulsification produced by the soda detracted from the merits of the mixture, making constant agitation of it necessary during use, and rendering a uniform distribution difficult. The amount of paraffin recommended for this wash was six volumes per cent., and the soap was reduced to 0·5 per cent., so as to minimise the bulk of solid thrown out when the soda was added. From such a mixture, the soda soap generally separates as a flocculent mass, which rises to the surface, mixed with the paraffin, and forms with it a bulky scum which occupies about one-third of the total volume. This scum, as will be shown below, is what may be termed a quasi-emulsion. It varies considerable in its nature according to the character of the soap used, and with one example of soap in our possession (although of the same brand as other samples) it is scarcely distinguishable from a true emulsion. (Caustic potash, it may be mentioned, cannot well be used as a substitute for caustic soda, on account of its price, and, if much soap is present, the soap is gelatinised, forming a magma which cannot be used for spraying.)

To avoid the disadvantages attaching to the separation of soap in these caustic emulsions, some more suitable emulsifier was sought. When quillaia or glue was used, the addition of caustic soda produced de-emulsification, and the same occurred to a slight extent with egg-albumen or starch; milk, also, is not very satisfactory, as it clots, even when caustic soda is not present. Attention therefore was turned to the possibility of obtaining an insoluble substance to act as emulsifier. This did not seem impracticable, from the fact that lime had recently been stated to produce emulsification.

Emulsions with Insoluble Emulsifiers.

Lime united with petroleum was first used for spraying purposes under the name of "limoid." A certain magnesian lime of a very fine-grained character was found to absorb double its weight of petroleum, and the mixture thus obtained, disseminated in three to nine times its volume of water, was used as a spray-fluid. Subsequently it was found that any ordinary lime would make an emulsion with petroleum, and the proportions recommended in America are 2·2 grams of quicklime to 11 c.c. of kerosene and 88 c.c. of water. There does not appear, however, to be any reason for adhering to these particular proportions, for they may be varied largely without materially affecting the results.

Much work was done on these lime emulsions before a clue was obtained as to their real nature, but only a brief reference to this work will be necessary here. Limes from various sources were examined, and all gave substantially the same results as calcium oxide prepared from marble, to which the following remarks apply.

On churning up lime with paraffin and water, a sort of emulsion is obtained, which either rises or sinks in the excess of liquid, according to the proportions used. The separation of the emulsion from the excess of water is much more rapid than in the case of emulsions in soap solutions. By suitably adjusting the proportions, an emulsion of a specific gravity of unity can be obtained; there is then no sinking or rising, so long as the proportion of water present is not more than 50 to 70 per cent., but, on dilution, part of the emulsion rises and part sinks; both these parts contain some oil, but the upper part most.

The volume occupied by emulsions with lime, and the percentage of oil contained in them, present no features analogous to emulsions in soap solutions, for here the lime itself occupies much of the total volume, and by its weight it drags down the oil and prevents any close-packing of the oil globules.

The general behaviour of these lime emulsions suggests that they are merely gross mechanical mixtures of lime and paraffin, and not true emulsions. An examination under the microscope confirms this view; the oil globules present in them are very large, and show great variations in size, being, under the most favourable conditions, ten times the diameter of the globules in a soap emulsion: they appear to be merely caught by, and entangled in, the particles of lime. Moreover, their size, instead of being practically constant, independent of the proportions of emulsifier and of oil, as in the case of soap emulsions, seems to be entirely dependent on them, and, if the lime is not present in considerable quantity, the globules are so large that they become visible to the naked eye, the liquid then being an evidently non-homogeneous mixture, which can claim no title to be called an emulsion. With a further reduction in the amount of lime, or an increase in that of oil, a separate layer of the latter appears.

In one series with "Water White" oil in proportions ranging from 1·5 to 67 per cent. by volume, and with lime equal to 2·2 grams CaO per 100 c.c. of the mixture, the product became visibly non-homogeneous when about 35 per cent. of paraffin was reached. A rather lower limit (about 30 per cent.) was obtained in a similar series with "Solar Distillate." In another series with the latter oil, where the paraffin was kept constant at 50 per cent., and the amount of lime varied, an apparently homogeneous emulsion was not obtained until the lime reached 10 grams per 100 c.c. of the mixture. With a very light oil, such as motor spirit, no homogeneous emulsions could be obtained at all, even when the percentage of lime exceeded that of the oil.

Other finely-divided substances have been examined, and found to give results similar to those with lime, although minor peculiarities are noticeable in the case of each substance; plaster of Paris, precipitated chalk, precipitated silica and alumina were amongst those which more closely resembled lime in their behaviour.

Mechanical mixtures of such substances with paraffin may conveniently be termed quasi-emulsions, for, with certain proportions between the solid and the paraffin, they approximate to emulsions in character, and may serve the same practical purposes as true emulsions do. Yet, as will be shown immediately, they are essentially different in constitution from true emulsions.

A quasi-emulsion with lime may be mixed with caustic soda without any change being produced, beyond rendering it somewhat more viscid, and it can be mixed with other insecticides and fungicides, notably with copper sulphate, thus giving it an advantage over emulsions with soap. On the other hand, it presents decided disadvantages, in the coarseness of the emulsion produced, the large porportion of lime required, and the difficulty of spraying it without clogging or destroying the nozzles of the machines

When copper sulphate was added to the lime before emulsification, it was noticed that the emulsion produced was altogether different from that with lime alone, and, following up this indication, it was ascertained that the basic sulphate of copper, precipitated by the action of the lime on the copper sulphate, is, by itself, capable of emulsifying paraffin and water, almost as finely as, and much more easily than, soap. If excess of lime is to be avoided, and all the copper is to be precipitated, the basic sulphate should be obtained by adding about 134 c.c. of lime-water to every gram of $CuSO_4,5H_2O$; if otherwise, solid lime may be added to the copper sulphate solution, and, although the quantity of pure lime required is only one-seventh of the weight of $CuSO_4,5H_2O$, it is advisable in practice to increase this to one-third if commercial lime is used, and to make this into a milk, running it through sacking into the copper sulphate, so as to eliminate any gross particles. On adding paraffin oil to this, and churning, one stroke of the syringe is sufficient to produce a perfect emulsion, and even shaking the mixture will form an emulsion good enough for practical purposes.

Such an emulsion possesses nearly all the characteristics of one made with soap, except that, there being a heavy and bulky solid present, the volume occupied by the emulsion proper does not depend solely on the oil globules, and the emulsion may rise or sink in the excess of solution according to the proportions of oil and basic sulphate used. It generally forms a very smooth cream, with a perfectly clear-cut line of division between it and the excess of liquid. In texture, it appears under the microscope to be identical with emulsions in soap, although the average size of the component globules is about twice as great. Nothing but a mass of oil globules can be seen, as the particles of basic sulphate are generally too small to be visible. If enough of the basic sulphate is present, the proportion of paraffin can be increased up to a very high point, the emulsions becoming thicker, until they are almost solid. With an insufficient proportion of basic sulphate, emulsification is imperfect; the minimum with strong emulsions of "Solar Distillate" is, approximately, 1 gram of $CuSO_4,5H_2O$, converted into basic sulphate, for every 120 c.c. of oil; if the emulsion is weak, the proportion of basic sulphate required is less. In the case of the sulphate of iron, which, as will be mentioned immediately, may be used in the same way, the proportions are of the same order of magnitude, 1 gram of $FeSO_4,7H_2O$ being required to emulsify about 200 c.c. of oil to make a 6 per cent. emulsion, 100 c.c. to make a 20 per cent. emulsion, and 30 c.c. to make a 60 per cent. emulsion.

To obtain satisfactory emulsions with the basic sulphates, it seems necessary to use a paraffin oil of high boiling point, such as a "Solar Distillate"; with ordinary lighting oil, emulsification is not perfect, unless the proportion of basic sulphate is very large, and with motor spirit the paraffin is never more than partially emulsified.

For practical purposes, an emulsion with basic copper sulphate presents many advantages over one made with soap. In the first place, it is a fungicide as well as an insecticide, for it contains all the elements of Bordeaux mixture; secondly, it is very bulky, and the tendency to separate from the liquid is much less. If the copper sulphate taken is 1·6 grams to 100 c.c. (the quantity used in "normal" Bordeaux mixture made with milk of lime), 3·5 c.c. of "Solar Distillate" (sp. gr. 0·858) makes with it an emulsion which neither sinks nor rises, and if the "Solar Distillate" is increased to 6 c.c., as it might be for winter use, or reduced to 1—2 c.c. for summer use, the tendency to rise or to sink, respectively, would be but small, the slightest agitation being sufficient to keep such emulsions disseminated throughout the liquid. With Bordeaux mixture made with lime-water, as recommended in the preceding communication (p. 1997), only 0·7 gram of copper sulphate to every 100 c.c. is used, and 1·4 c.c. of "Solar Distillate" will make this into an emulsion which will neither sink nor rise, and which is of a most convenient strength for general summer use.

Besides the facility and certainty with which these emulsions can be made, they possess the advantage of being much more permanent than emulsions made with soap. No single instance has yet occurred in which any one of them has de-emulsified spontaneously. Also, they can be mixed with caustic soda (2 per cent. being generally used) to make a detergent winter wash, without becoming de-emulsified, as in the case of soap emulsions.

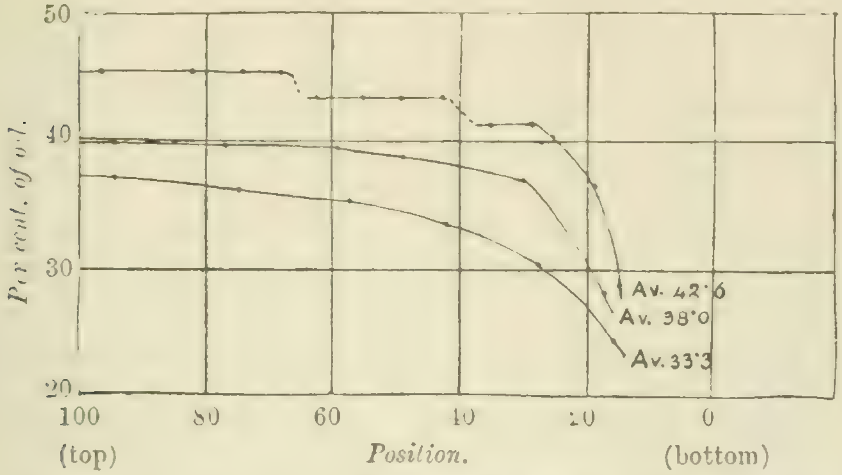
In connexion with the use of soda with these emulsions, one or two points must be mentioned. Copper hydroxide will not emulsify paraffin as the basic sulphate does, and, although caustic soda precipitates the basic sulphate $4CuO,SO_3$ when added in the proper proportions, excess of alkali converts it into the hydroxide, so that soda cannot be used for the preparation of a caustic copper emulsion. But if the $4CuO,SO_3$ is precipitated by lime, and then emulsified, the excess of soda may be added without producing any appreciable change; it is only after the lapse of a month or more that an emulsion made in this way will show any signs of the presence of copper hydroxide, and begin to blacken. This difference in behaviour, according to which alkali is used for the precipitation, naturally caused much perplexity, until the investigation of the basic sulphates, detailed in a previous communication, had shown that the precipitate with lime is not merely $4CuO,SO_3$, but a compound of that sulphate with calcium sulphate.

If fungicidal properties are not required in the caustic wash, ferrous sulphate may be substituted for the more expensive copper sulphate. The emulsions with the iron salt have certain advantages over those with the copper salt. The oil globules in them are smaller (about one-third to one-fifth of the diameter) and the emulsions are more bulky, and separate from the excess of liquid more slowly. Moreover, ferrous hydroxide, unlike copper hydroxide, is itself capable of emulsifying, and hence the precipitation with lime may be dispensed with and the caustic soda alone be used. A much finer emulsion, however, is obtained if lime is used as the precipitant, as in the case of copper. Where soda is used, that required for the precipitation, as well as the extra 2 per cent., may all be added to the iron sulphate at once before emulsifying with paraffin. The basic ferrous sulphate, or ferrous hydroxide, as the case may be, is, of course, partially oxidised, and the emulsion becomes nearly black. On keeping it in a closed vessel, it sometimes (especially if excess of lime is present) becomes almost colourless, organic substances in the paraffin apparently reducing the ferric compounds; on exposure to air, it becomes orange-red, ferroso-ferric oxide being formed. These changes do not appear to affect the emulsification.

One drawback to the copper emulsion is that it cannot be prepared in a concentrated form like a soap emulsion. The percentage of oil present may be increased, but not that of the copper, for lime must be used as the precipitant, and, if this is added to a strong solution of copper sulphate, the precipitated basic sulphate forms a compact mass which will not emulsify the oil properly. With ferrous sulphate, however, where soda can be used as the precipitant, this difficulty does not exist, and it is possible to make an emulsion of which 100 c.c. contain 60 c.c. of oil, this being ten times the strength generally required for spraying. The amount of iron which can be got into such a strong emulsion, however, is not large, and, consequently, the emulsion is light, and rises rapidly to the surface when diluted, necessitating agitation during use.

Some of the copper emulsions were examined by analysis in the same way as soap emulsions. It will be sufficient to quote the results with one of them only, and these are given in the accompanying table and in Fig. 2. The mixture taken for emulsification contained 20 c.c. of "Solar Distillate" and 0·18 gram of CuO, in the form of sulphate, per 100 c.c. Portions of the emulsion proper were analysed throughout their mass after twenty-four hours, ten days, and twelve weeks, the average proportions of oil in them then being 33·3, 38·0 and 42·6 per cent., respectively. The emulsion becomes more concentrated as time elapses, and, at the same time, the curve representing its composition becomes flatter, although in all cases there is a rapid fall in concentration towards the bottom of the column. The most marked feature, however, is the ultimate arrangement of the emulsion into layers of uniform composition, which, although not visible as separate layers to the eye, are made evident by the analysis. Such an arrangement has already been noticed in the case of emulsions with soap. As will be seen from the table, the percentage of basic sulphate in the emulsion decreases from the top to the bottom with the percentage of oil, but not so rapidly as the latter, so that the proportion of it

FIG. 2.



Composition of emulsions. "Solar Distillate" with basic copper sulphate.

Composition of Emulsions of "Solar Distillate" with Basic Copper Sulphate.

After 24 hours.		After 10 days.		After 12 weeks.			
Position.	% Oil.	Position.	% Oil.	Position.	% Oil.	% CuO.	CuO : Oil.
100—83	36·8	100—85	40·1	100—93	45·3	0·408	0·907 : 100
83—66	36·0	85—69	39·9	93—86	43·5		
66—50	35·4	69—53	39·4	86—79	45·3		
50—34	33·5	53—37	38·7	79—72	45·3		
34—19	30·1	37—22	36·7	72—66	45·3		
19—7	22·8	22—8	26·4	66—60	43·4	0·394	0·916 : 100
				60—53	43·3		
				53—47	43·1		
				47—39	43·3		
				39—31	41·3	0·378	0·928 : 100
				31—25	41·3		
				25—22	40·0		
				22—17	37·2	0·352	1·071 : 100
				17—11	28·5		

to the oil increases downwards. It is noticeable, however, that this increase is very small; in spite of the differences in specific gravities, about 2·5 and 0·86, there is very little separation of these two substances, and the union between them must, therefore, be of a decidedly intimate character.

The Nature of Emulsions.

It is evident that emulsions with basic copper sulphate are strictly similar in nature to those with soap, and are quite different from the quasi-emulsions with lime. Many other substances act in a manner similar to basic copper sulphate, but few of them so satisfactorily. The action, however, is not distinctive of basic salts, some of them, such as the basic sulphates of copper, iron and nickel, form true emulsions, whereas those of zinc, aluminium and cadmium form quasi-emulsions only; other substances when freshly precipitated behave in a similarly arbitrary manner, calcium arsenate, for instance, forms a good emulsion, whereas with barium sulphate, no signs of emulsification are obtained. On the other hand, no connexion between emulsification and the nature of the metal present can be traced; copper hydroxide will not emulsify, although the basic sulphate will, whereas both ferrous hydroxide and basic ferrous sulphate are good emulsifiers. Nor is the mere bulkiness of the precipitate any guide to its emulsifying powers; precipitated aluminium silicate, although very bulky, does not emulsify, nor does gelatinous silica. The colloidal condition of the substance, also, has no influence on the results, for paraffin will not emulsify in a dialysed solution of silica.

The view which the writer was eventually led to adopt as to emulsification, was that it depended solely on the size of the particles constituting the precipitate. When the oil is broken up into small globules by being forced through the syringe, and these globules find themselves in the presence of a number of very much more minute solid particles, the latter will be attracted by the globules, and will form a coating or pellicle over the globules, preventing them from coming in contact and coalescing with their neighbours. Whether gravitation alone is sufficient to account for such a result, or whether other forces come into play, must be left for others to determine, but that the solid particles do congregate closely round the globules, there can be no doubt, for they can often be seen under a powerful microscope. With basic copper sulphate this is so, although the particles are so nearly ultra-microscopic that they cannot be resolved sufficiently to admit of any estimate being made as to their actual size; with basic iron sulphate, they are still smaller, and quite invisible, but their aggregation round the globules is evident from the brown ring encircling the latter.

Further evidence that the globules must be enveloped in some covering is found in the fact that these emulsions do not make the containing vessel oily; indeed, this forms a very good distinctive test between a true emulsion and a quasi-, or imperfect, emulsion. The same test may be varied by dropping a little of the liquid into a basin of water; if unemulsified paraffin is present, the surface of the liquid becomes oily, but not so if the paraffin is present as a true emulsion.

An emulsion on this view, however much it is diluted with water, will suffer no de-emulsification, whereas with a quasi-emulsion, where we simply have oil globules entangled with the gross particles of a solid, it should always be possible to separate the greater part of the oil by adding enough water. This, as a matter of fact, is found to be the case. It is also possible to remove the oil from a substance with which it forms only a quasi-emulsion, by adding another substance with which it forms a true emulsion. Thus a quasi-emulsion of lime and paraffin of a suitable strength will rise in a mass to the surface of water, but, if some sodium arsenate is added, calcium arsenate is formed, and, as this is a true emulsifier, it forms an emulsion with the oil, and rises to the surface, whilst the lime, deprived of the oil, sinks to the bottom.

Neither in the case of a true emulsion nor in that of a quasi-emulsion does the nature of the menstruum appear to have any influence on the emulsification, so long as it does not react chemically with the emulsifier or the oil; a variety of salts may be dissolved in water containing an emulsifier without affecting the emulsion, beyond making it in some cases (notably when caustic soda has been added) more viscid, due, no doubt, to an increase in the coefficient of friction. Even strong mineral acids have no effect in a case such as that of clay (some clays will act as emulsifiers), where the solid emulsifier is insoluble in acids.

Although emulsions and quasi-emulsions are radically different in their nature, various substances will yield results showing every possible gradation between the two, for the simple reason that substances may consist of particles of every gradation of magnitude, some small enough to emulsify the oil globules, and others too large to do more than form quasi-emulsions. In the same way, there is every gradation between a quasi-emulsion and the complete separation of the oil and water into independent layers.

The power of emulsifying, not being an inherent property of the substance, but simply depending on the size of its particles, it follows that this power should be destroyed by aggregation; that this is so, can easily be proved. The basic sulphates, calcium arsenate, Oxford clay, &c., all of which form true emulsions, are found to be quite incapable of doing so after they have been dried, however finely they may then be powdered.

The average size of the globules in an emulsion seems to be dependent on the size of the particles of the emulsifier. Thus the particles of basic ferrous sulphate are more minute than those of basic copper sulphate, and the emulsion is decidedly finer-grained also; with nickel basic sulphate, both the particles and the oil globules are of about the same size as with the copper salt, whereas with cadmium and zinc basic sulphates the particles are gross and the emulsion is very coarse, being to a large extent only a quasi-emulsion. Whether, however, the chemical nature of the emulsifier is altogether without effect on the results or not, and whether the size of the particles is the sole determining factor, it is impossible to decide with certainty, without a more extended series of observations, aided by better eyesight and better microscopic appliances than were available in the present case. It seems, however, that the attraction between the oil globules and the solid particles may be sufficient to modify somewhat the chemical behaviour of the latter. The basic sulphate of copper precipitated by lime, when treated with excess of caustic soda, will blacken after a few weeks, owing to the formation of copper oxide, but, when emulsified with "Solar Distillate," this blackening does not commence nearly so soon; it is more rapid when a lighting oil is used, this forming a coarser emulsion, and much more so if petrol is used, when the emulsification is very imperfect indeed. Similar evidence is obtained by making emulsions with the same oil, but using different proportions of it; that which contains more oil will blacken more slowly. Analogous results are obtained with ferrous sulphate, the colour of the emulsions, due to different degrees of oxidation, differing according to the nature of the oil used. It is possible, however, that in these cases the retardation of the action of the soda on the basic sulphate, or the oxidation of the compounds present, may be due to a chemical action of impurities in the oil.

A few instances exist which seem at first sight to negative the view that the power of emulsifying is conditioned by the size of the solid particles. Thus, precipitated sulphur, purple of Cassius, and ferric ferrocyanide, all of which are in an extreme state of sub-division, will not emulsify paraffin at all. The behaviour of sulphur gives a clue to this result. When flowers of sulphur, thoroughly incorporated with water, are churned with paraffin, the latter abstracts the whole of the sulphur from the water, forming with it a greasy mixture, which sticks obstinately to the syringe, containing vessel, &c., the paraffin evidently wetting the sulphur in a way which the water does not. A similar effect is observed in the case of purple of Cassius and ferric ferrocyanide; although the paraffin is not emulsified at all, it abstracts the whole of these substances from the water, becoming intensely coloured by them, and leaving the water colourless, just as if they dissolved in the paraffin. The view therefore that emulsification depends solely on the minuteness of the solid particles must be so far modified as to apply only to such solids as are wetted more easily by water than by oil, otherwise there is no emulsification at all.

The explanation of emulsification here advanced would hardly be acceptable unless it could be applied equally to cases where the emulsifier is a liquid, and there seems to be but little difficulty in doing so; for these liquid emulsifiers are all substances which, under the conditions obtaining, partly separate from the solution, and yield sufficient solid particles to form a pellicle over the oil globules. Liquid emulsifiers are all distinguished, so far as we know, by a feeble affinity for water; in many cases they are, or contain, protein substances, which, as Ramsden has shown, form a skin of solid matter at any boundary between the solution and another fluid, whether liquid or gaseous. In other cases, the deposition of some particles of the solid would result from this solid being insoluble in the paraffin. The water in the neighbourhood of a paraffin globule would become impregnated with paraffin, and the dissolved substance, having but a small affinity for water, would be thrown out of solution. Solutions of egg-albumen, glue and starch, when covered with a layer of paraffin, all form a slight opaque film at the junction of the two liquids. In this way, each globule of oil would obtain for itself the solid particles necessary for its emulsification; but these particles would, no doubt, often be redissolved, whilst others, in their turn, would be deposited, and, in the course of such changes, opportunities would occur for the coalescence of neighbouring globules. This explains why emulsions in soap will generally de-emulsify spontaneously, if left long enough, whereas emulsions with a really insoluble emulsifier seem to be quite permanent.

Formed in this way by solid deposited *in situ*, an emulsion in soap, or similar substances, would naturally be more fine-grained, and the globules would be more closely packed, than in cases where a separately formed precipitate is the emulsifier. A rise of temperature, or an increase in the volatility of the oil used, would result in the soap solution becoming more permeated with paraffin particles, and depositing more of the dissolved soap, thus facilitating emulsification. With soap, a rise of temperature does facilitate emulsification, and an increase in the volatility of the oil sometimes does the same (pp. 2002, 2006). With insoluble emulsifiers, however, neither a rise of temperature nor an increase in volatility favours emulsification, indeed, the latter materially hinders it (p. 2009), owing, no doubt, to the more volatile oils being more mobile.

Whether any soluble inorganic substance exists which would emulsify oil in the same way as does soap, appears to be very doubtful; it is certainly probable that any substance which is crystalline would be incapable of emulsifying. Saturated solutions of calcium hydroxide and sulphate, as well as of sucrose, dextrose and dextrin, have been tried, with negative results.

With soap, the particles requisite for emulsification are also provided in another way; for when soft soap is dissolved in much water, or when a strong solution of it is diluted, a considerable amount of a very fine deposit is obtained, and this is often in such a minute state of division that it remains suspended in the liquid for weeks. The separation of this precipitate on dilution, and its redissolution or concentration, explains a fact previously noticed (p. 2002), which otherwise would present considerable difficulty, namely, that for each proportion of paraffin and water the amount of soap necessary for emulsification must not only be in excess of a certain minimum, but also must not be in excess of a certain maximum. The existence of the superior limit is explained if the emulsification depends to any large extent on the presence of solid particles precipitated by dilution, for the tendency to deposit such particles would be less in stronger than in weaker soap solutions.

(It should be mentioned, however, that a superior limit does not seem to exist in the case of all soaps. This is not surprising, for soaps vary largely in composition, even when they are of the same brand, and from the same factory, and they differ considerably in their behaviour on dilution.)

That the formation of a pellicle of solid particles over the oil globules affords an explanation of emulsification, is, as has been mentioned, the conclusion to which Dr. Ramsden also was led, and the view that such a pellicle exists in the case of the oil globules in milk was advocated long ago. So far as can be seen, this view seems to harmonise with all the observed facts.

Behaviour of Various Substances.

It would be tedious and unprofitable to describe at length the behaviour of the many substances which have been examined as regards their emulsifying powers; but they may be briefly enumerated, classing them roughly into those which give true emulsions, those which give imperfect emulsions or quasi-emulsions, and those which do not seem to emulsify at all. In some cases, however, it is rather difficult to decide in which class to place a particular substance, and, in others, the method of preparation affects the behaviour of the substance in question.

Good Emulsifiers.—Amongst soluble, or partially soluble, substances, soft soap seems to be the best; dissolved starch, milk and flour are good, although the latter forms a flocculent, and not a creamy, emulsion, and milk gives rise to solid clots; glue emulsifies well, and so does egg-albumen, but the emulsion with the latter is rather frothy, owing to enclosed air bubbles; saponin and quillaia bark give good emulsions when the proportion of oil present is not large.

Amongst insoluble emulsifiers, the basic sulphate of iron is the best, followed by those of copper and nickel; the basic sulphates of zinc and aluminium generally give good emulsions at first, but aggregation of the particle seems to occur, and causes partial de-emulsification. Ferrous hydroxide and the higher oxides of iron (hydrated) are good. The precipitate obtained by adding sodium carbonate to copper sulphate is a very good emulsifier, so are calcium carbonate and calcium arsenate when first precipitated, but the latter soon become crystalline, and de-emulsification follows; lead arsenate, freshly precipitated, is good, and zinc oxychloride, or basic chloride, is fair, although the emulsion with it is flocculent; some fine clays (unheated), such as Oxford clay, give good emulsions, but they, naturally, contain many gross particles which sink to the bottom unemulsified; ferrous hydrosulphide gives a good emulsion if the proportion of oil present is small.

Substances producing Quasi-Emulsions, or producing Partial Emulsions.—Lime, silica, alumina, plaster of Paris and many fine powders which have been dried; also the following precipitated substances when in the liquids from which they have been precipitated: basic cadmium sulphate, magnesium hydroxide, copper hydroxide, the basic sulphates of zinc and aluminium, stannous oxychloride, purple of Cassius, lead arsenate paste (a commercial preparation for insecticidal purposes), some clays and brick-earths, copper hydrosulphide, ferrous hydrosulphide (unless the proportion of paraffin is very low), and precipitated soda soap.

Substances showing little or no Power of Emulsifying.—Precipitated lead chloride, lead sulphate, barium sulphate, neutral silica solution, sulphur precipitated by adding acid to sodium thiosulphate, flowers of sulphur and dried Paris-green (in both of which cases the powders seem to absorb the oil, forming a sticky mass which adheres to the syringe and containing vessel in an obstinate manner); an alcoholic solution of resin precipitated by water, ferrous ferricyanide, ferric ferrocyanide, and purple of Cassius (in the last two cases the precipitate is carried up by the oil in sufficient quantities to colour it strongly); and, lastly, any coarse, or even fine, powders, especially when present in small proportions.

Summary.

When paraffin oil is churned up with a solution of soft soap, an emulsion is formed which rises to the surface and generally contains 65 to 82 per cent. by volume of oil. Emulsions containing as much as 99 per cent. can, however, be obtained, and these are so stiff as to be almost solid. The character of the oil does not much affect the results, neither does the extent of the churning nor the proportion of soap, so long as this proportion is within certain limits.

The amount of oil in an emulsion which has arrived at a state of equilibrium decreases somewhat from the top downwards, but there is often a tendency to arrange itself in layers of approximately uniform composition.

Solutions of other organic substances, such as glue, flour, milk, starch, albumen, saponin, &c., act as emulsifiers for paraffin oil. All these emulsions will often spontaneously become de-emulsified, and this occurs at once if the emulsifier is destroyed; for example, if an acid or any sodium salt is added to an emulsion with soap. Electrolytes, as such, seem to have no de-emulsifying action. The addition of unemulsified paraffin to an emulsion will gradually de-emulsify the whole.

The oil globules in an emulsion are probably prevented from coalescing by being enveloped in a pellicle consisting of particles of solid much more minute than the globules themselves. The solid particles would be derived from the solution, which in all cases contains a substance with but little affinity for water, and insoluble in paraffin, it being, therefore, precipitated in the neighbourhood of the paraffin globules.

Apparently, a precipitate consisting of any insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier, and in some cases it is possible under a microscope to see the coating of solid particles which envelop the oil globules. Emulsions made with an insoluble emulsifier are in every respect similar to those made with soap, &c., except that they never seem to de-emulsify spontaneously; spontaneous de-emulsification being, no doubt, due to the fact that the solid particles, as in the case of soap, are soluble in water, and are continually being redissolved and reprecipitated, thus affording opportunities for the coalescence of the oil globules.

The basic sulphates of iron and copper are amongst those substances which give excellent emulsions. They may be formed by adding lime, or lime-water, to the normal sulphates, and then the paraffin, when the slightest churning, or even shaking of the mixture, produces emulsification. Besides the ease of manufacture, and the absence of spontaneous de-emulsification, these emulsions possess the advantage of not being decomposed by the addition of caustic soda, as are emulsions with soap, and caustic soda is required when the emulsion is used as a winter wash for trees. When the copper salt is used, the emulsion possesses all the fungicidal properties of Bordeaux mixture.

Many other precipitated substances act as emulsifiers, but this property is destroyed as soon as they have been dried, or have by any other means been deprived of their fine-grained structure.

Solids which are not sufficiently fine-grained to emulsify will, in many cases, when present in considerable proportions, form quasi-emulsions. In these, the particles of oil are merely entangled with the particles of solid, and may be separated from them by such simple means as dilution with water. Lime is an instance of a substance which forms a quasi-emulsion which can be used for spraying purposes. Other substances, including many recently-formed precipitates, and, probably, all crystalline solids, seem to be incapable of forming even quasi-emulsions.

CXCVII.—*The Electrolytic Preparation of Disulphides. Part I. Dibenzyl Disulphide and Diethyl Disulphide.*

By Thomas Slater Price and Douglas Frank Twiss.

In a preliminary note (Proc., 1906, **22**, 260), we have shown that the electrolysis of a solution of sodium benzyl thiosulphate yields *dibenzyl disulphide.* The electrolysis was carried out in a beaker, the cathode consisting of a sheet of platinum foil lying close to the sides of the beaker, the anode being a piece of stout platinum wire. This apparatus was used because it was thought that the electrolysis would probably take place in a similar manner to that of sodium acetate, a high current density at the anode being necessary:

$$2CH_3\cdot CO_2 \longrightarrow C_2H_6 + 2CO_2.$$
$$2C_6H_5\cdot CH_2\cdot S\cdot SO_3 \longrightarrow (C_6H_5\cdot CH_2)_2S_2 + 2SO_3.$$

When a pure aqueous solution of sodium benzyl thiosulphate was used, the solid dibenzyl disulphide obtained was contaminated by a quantity of a pungent oil, which, from its behaviour towards the air, was benzyl mercaptan. The formation of the latter was probably due to the decomposition of some of the complex thiosulphate by acid formed during the electrolysis. The addition of sodium bicarbonate or carbonate, in quantity sufficient to neutralise any acid formed, completely prevented the formation of any mercaptan, and the only product was then a white solid, which investigation proved to be dibenzyl disulphide. Consequently, in all later electrolyses, an equivalent weight of sodium carbonate was added to the complex thiosulphate taken.

All the earlier experiments were carried out in the apparatus described, that is, in an undivided cell, and the results were so good, yields amounting to even 80 per cent. of the theory (calculated on the thiosulphate compound taken) being obtained, that it was assumed that the action was exactly as had been anticipated. However, on placing the thiosulphate compound in the anode chamber of a divided cell, it was found that no disulphide was formed, whereas on carrying out the electrolysis with the thiosulphate compound in the cathode compartment, the usual yield of the disulphide was obtained. The formation of the disulphide is thus due to reduction at the cathode, hydrogen sulphite ions being produced at the same time according to the equation:

$$2C_6H_5{\cdot}CH_2{\cdot}S{\cdot}SO_3' + 2H \longrightarrow (C_6H_5{\cdot}CH_2)_2S_2 + 2HSO_3'.$$

One would be inclined to suppose that the product of reduction at the cathode would be the mercaptan, since it is usually stated that disulphides are very readily reduced, but in none of the experiments where platinum electrodes and an equivalent quantity of sodium carbonate were used has any mercaptan, as indicated by the odour, been formed. This has also been the case in a few experiments where a lead cathode, at which electrochemical reductions generally take place much more readily than with platinum electrodes, has been used. Fichter and Bernoulli (*Zeitsch. Elektrochem.*, 1907, **13**, 310) have found that the reduction of *p*-toluenesulphonyl chloride to *p*-tolyl mercaptan takes place quantitatively when lead cathodes and a low current density are used; electrodes of nickel or platinum did not give such good results.

In the present case, it seems as if the $C_6H_5{\cdot}CH_2{\cdot}S{\cdot}$ residue, which is formed when the link between the two sulphur atoms in the sodium benzyl thiosulphate is broken, combines with another such residue before reduction to the mercaptan can take place. That the two residues will unite in this manner was shown by Bunge (*Ber.*, 1870, 3, 295, 911), who prepared disulphides (ethyl, amyl, and phenyl) by the electrolysis of alcoholic solutions of the sodium mercaptans. The disulphides were formed at the anode.

Further experiments to find out the conditions necessary to obtain the best results showed that, when the pure sodium benzyl thiosulphate is used, there is no great advantage in having the anode and cathode in separate compartments, so that the apparatus required is very simple. Also, the yield of disulphide is improved by using a concentrated solution, a low current density at the cathode, and a temperature of 60—70°. As will be seen from the figures given in the experimental part, the lower the current density at the cathode the better is the yield of disulphide, but, since with very low current densities the time necessary for electrolysis is unduly prolonged, it is convenient to use a current density of about 1 ampere per sq. dcm., and to pass more than the theoretical current. The conditions for the electrolysis may be summarised as follows. For the electrolysis of sodium benzyl thiosulphate, a concentrated aqueous solution (5 grams in 30 c.c. of water) is used in which an equivalent quantity of sodium carbonate (3·16 grams) has been dissolved. The mixture is warmed to 60—70° and 50 per cent. more than the theoretical current (theory = 0·593 ampere-hour) is passed, using a cathode current density of approximately 1 ampere per sq. dcm. The disulphide is collected and recrystallised once from alcohol, a pure product being then obtained.

Diethyl disulphide may be prepared in a similar manner from sodium ethyl thiosulphate, but, being a liquid, it is extracted with ether and purified by distillation.

Since the isolation of the pure sodium benzyl thiosulphate is a somewhat tedious process, experiments were next carried out to find whether the mixture obtained by heating together the alcoholic solution of benzyl chloride and aqueous sodium thiosulphate could be directly electrolysed with good results. Since the mixture contains sodium chloride together with sodium benzyl thiosulphate, it was necessary to use a divided cell for the electrolysis, otherwise the chlorine liberated at the anode might enter into reaction with other substances in solution; the anode solution was sodium carbonate. The results were quite satisfactory, a yield of more than 80 per cent. being obtained, especially when the solution was kept well stirred by continuous rotation of the cathode.

Diethyl disulphide may be also prepared by the electrolysis of the mixture obtained from the interaction of ethyl iodide and sodium thiosulphate. A yield of about 50 per cent. was obtained. Only one such experiment was carried out, a rotating cathode being used, and the conditions necessary for obtaining a good yield were not further investigated. It is noteworthy that, although in this case the disulphide is a liquid and remains in solution (which contains alcohol) to some extent, there does not seem to be any appreciable formation of mercaptan. The disulphide, as it is produced, remains distributed throughout the liquid in the form of fine drops, owing to the action of the rotating cathode, but it does not seem to be reduced, whereas *p*-toluenesulphonyl chloride is reduced to the mercaptan under such conditions.

At present, no further experiments have been carried out to find under what conditions disulphides may be reduced to mercaptans, as we have confined our attention to the formation of disulphides. It is possible that further investigations on the velocity of reduction of sodium benzyl thiosulphate under known cathode potentials may lead to interesting results.

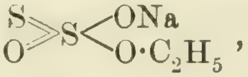
The formation of disulphides by electrolysis throws light on the constitution of thiosulphates. Bunte in his original communication on sodium ethyl thiosulphate (*Ber.*, 1874, **7**, 616) pointed out that the formation of ethyl mercaptan by the decomposition of sodium ethyl thiosulphate by acids was in agreement with the formula :

$$NaO\cdot SO_2\cdot S\cdot C_2H_5,$$

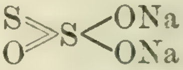
from which it follows that the formula of sodium thiosulphate is

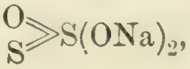
$$NaO\cdot SO_2\cdot SNa.$$

This is also supported by the results of the electrolytic reduction of the salt, since it is difficult to imagine how a disulphide could result from the electrolytic reduction of a compound having the formula :



$$\begin{matrix}S\\O\end{matrix}\!\!>\!S\!<\!\begin{matrix}ONa\\O\cdot C_2H_5\end{matrix},$$

which is deduced from the alternative formula  $\begin{matrix}S\\O\end{matrix}\!\!>\!S\!<\!\begin{matrix}ONa\\ONa\end{matrix}$ for sodium thiosulphate. Gutmann (*Ber.*, 1905, **38**, 1728 and 3276 ; 1906, **39**, 509 ; 1907, **40**, 3614), from a study of the action of sodium arsenite (and potassium cyanide) on tri- and tetra-thionates, arrives at the conclusion that the formula for sodium thiosulphate is



$$\begin{matrix}O\\S\end{matrix}\!\!>\!S(ONa)_2,$$

His reasons are as follows. When sodium tetrathionate reacts with sodium arsenite in alkaline solutions, the reaction takes place according to the equation :

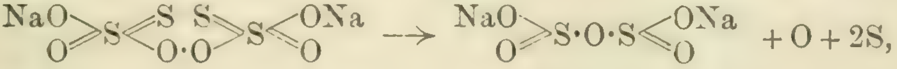
$$Na_2S_4O_6 + 3Na_3AsO_3 + 2NaOH = 2Na_3AsSO_3 + Na_3AsO_4 + 2Na_2SO_3 + H_2O$$

$$\text{or } S_4O_5 = 2S + O + 2SO_2 ;$$

two molecules of monosulphoxyarsenate, one of arsenate, and two of sulphite being formed. According to Gutmann, this cannot be explained by Mendeléeff's formula for tetrathionate, namely, $NaO\cdot SO_2\cdot S\cdot S\cdot SO_2\cdot ONa$, which is derived from the formula:

$$O_2S(ONa)(SNa)$$

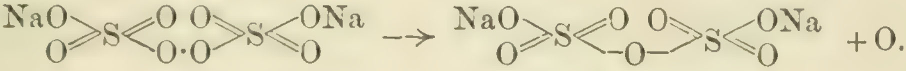
for sodium thiosulphate. If, however, thiosulphate is given the isomeric form $\substack{S\\O}\!\geqslant\!S(ONa)_2$, the formula for tetrathionate would then be $\substack{NaO\\O}\!\geqslant\!S\!<\!\substack{S\quad S\\O\cdot O}\!\geqslant\!S\!<\!\substack{ONa\\O}$, that is, a derivative of persulphuric acid. The above reaction could then be explained, thus:



$$\substack{NaO\\O}\!\geqslant\!S\!<\!\substack{S\quad S\\O\cdot O}\!\geqslant\!S\!<\!\substack{ONa\\O} \longrightarrow \substack{NaO\\O}\!\geqslant\!S\cdot O\cdot S\!<\!\substack{ONa\\O} + O + 2S,$$

Sodium pyrosulphite.

corresponding with



$$\substack{NaO\\O}\!\geqslant\!S\!<\!\substack{O\quad O\\O\cdot O}\!\geqslant\!S\!<\!\substack{ONa\\O} \longrightarrow \substack{NaO\\O}\!\geqslant\!S\!<\!\substack{O\quad O\\-O-}\!\geqslant\!S\!<\!\substack{ONa\\O} + O.$$

Sodium pyrosulphate.

The formula $\substack{S\\O}\!\geqslant\!S(ONa)_2$ is, however, not in accordance with our results, and, moreover, it would lead to the formula $OS(ONa)_2$ for sodium sulphite, instead of the generally accepted formula:

$$Na\cdot SO_2\cdot ONa.$$

The authors are, however, of the opinion that Gutmann's results can be explained by Mendeléeff's formula for sodium tetrathionate.* Although not explicitly stated, Gutmann's contention seems to be, that the two residues, $\cdot SO_2\cdot ONa$, which, according to Mendeléeff's formula would be left after the withdrawal of two atoms of sulphur from a molecule of tetrathionate, should unite with the formation of a molecule of dithionate; the dithionate would not then give arsenate and sulphite, since dithionates have no action on arsenites.

Now, Friessner has shown (*Zeitsch. Elektrochem.*, 1904, **10**, 265) that dithionate is formed at the anode when neutral or alkaline solutions of sodium sulphite are electrolysed, and that the process is represented by the equation $2SO_3'' + O + H_2O = S_2O_6'' + 2OH'$, and not by the expression $2SO_3'' + 2\oplus \longrightarrow S_2O_6''$; that is to say, sulphite ions do not condense directly with the formation of dithionate ions.

The reversal of the first equation would give the two sulphite ions and the one atom of oxygen necessary for the formation of arsenate; two hydroxyl ions (that is, 2NaOH) being used up at the same time as required by Gutmann's results. Dithionates, however, are not decomposed by boiling with alkalis, so that the equation does not seem to be reversible; but in the decomposition of tetrathionate, after the two sulphur atoms are removed, the two residues, $\cdot SO_2\cdot ONa$, would not combine to form dithionate (see above), and would in all probability react according to the equation :

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* The alternative formula of Debus, namely, $NaO\cdot SO_2\cdot S\cdot O\cdot SO_2\cdot SNa$, has not been taken into consideration, since Hertlein has shown (*Zeitsch. physikal. Chem.*, 1896, **19**, 287) that it does not accord with the experimental facts nearly so well as that of Mendeléeff.

$$2\ SO_2\cdot ONa + 2NaOH = 2Na_2SO_3 + H_2O + O\ .\ .\ .\ .\ (A)$$

which is in reality the reverse of the above equation. This at the same time probably explains why two molecules of sodium hydroxide are necessary in Gutmann's equation.

A similar explanation will hold for the action of potassium cyanide on sodium tetrathionate. Gutmann found that the reaction was expressed by the equation :

$$Na_2S_4O_6 + 2KCN + 2NaOH = 2KCNS + Na_2SO_4 + Na_2SO_3 + H_2O.$$

In this case, the free atom of oxygen shown in the equation (A) oxidises one of the molecules of sodium sulphite to sodium sulphate.

Gutmann further found that sodium trithionate acts on sodium arsenite in alkaline solution according to the equation :

$$Na_2S_3O_6 + 2Na_3AsO_3 + 2NaOH = 2Na_2SO_3 + Na_3AsSO_3 + Na_3AsO_4 + H_2O$$

$$\text{or}\ \ S_3O_5 = 2SO_2 + S + O.$$

This also is in accordance with the formula : $NaO\cdot SO_2\cdot S\cdot SO_2\cdot ONa$ for sodium trithionate.

The latest published results of Gutmann (*Ber.*, 1907, **40**, 3614) on the action of alkalis on sodium tetrathionate are explained equally as well by Mendeléeff's formula as by that put forward by Gutmann.

EXPERIMENTAL.

Electrolysis of Pure Sodium Benzyl Thiosulphate.—In these experiments, the current was registered by an ammeter and was maintained constant by means of a variable resistance in the circuit ; the total current passed was measured by a copper coulometer. The solution was stirred from time to time during the electrolysis, and an undivided cell was used.

The following table shows the improved yield obtained by the addition of sodium carbonate or bicarbonate. In the first experiment, the pure solution of the substance was electrolysed, whilst in the second and third, equivalent quantities of sodium carbonate and bicarbonate were respectively added. Five grams of sodium benzyl thiosulphate were used in each case, and the volume of the solution was 50 c.c. The current is given in terms of that theoretically required for the complete reduction of the substance, and the yields are expressed as percentages of those theoretically expected from the weight of substance taken. The yields were obtained by filtering the crude disulphide into a Gooch crucible, washing well with water, and then drying to constant weight in a vacuum desiccator. The crude disulphide was practically pure, the melting point scarcely altering on recrystallisation. The current density (C.D.) is expressed in amperes per sq. dcm.

Current, per cent.	C.D.	Yield, per cent.
107·6	1·27	35·3
106·5	1·27	61·4
97·14	1·27	61·8

The following table shows the effect of variation of (1) the concentration of the solution, (2) the temperature, (3) the current density at the cathode. In each case, 5 grams of the thiosulphate compound were taken and the equivalent quantity of sodium carbonate added.

No.	Current,* per cent.	C.D.	Volume of solution.	Temp.	Yield, per cent.
1	107·2	1·27	30 c.c.	15°	93·8
2	106·5	1·27	50 ,,	15	61·4
3	99·4	1·27	100 ,,	15	42·7
4	107·6	1·27	200 ,,	15	41·9
5	102·7	1·27	50 ,,	70	73·5
6	105·2	1·27	50 ,,	70	81·6
7	100·4	2·54	50 ,,	15	46·3
8	118·1	96·0	50 ,,	15	18·0

* In each case, the amount of current passed was 100 per cent., according to the ammeter reading, but, since the resistance in the circuit has to be altered from time to time in order to keep the current constant, the correct number of ampere-hours cannot be obtained from the ammeter reading, but only from the copper coulometer.

Experiments 1 to 4 show that an increase in the concentration improves the yield, whilst a comparison of 2, 5, and 6 shows the beneficial effect of a higher temperature. The difference in the yield in experiments 5 and 6 is due to the fact that the beaker in the latter experiment was covered with a clock glass, thus preventing the volatilisation of disulphide which took place in experiment 5 with an open beaker.

Experiments 2, 7, and 8 show clearly that a low current density is favourable to the production of the disulphide. This is what might be expected, since with a high current density a large amount of hydrogen would escape, without exerting its reducing action on the complex thiosulphate.

In order to investigate more thoroughly the effect of current density, the actual amount of hydrogen liberated at the cathode was measured, and compared with the amount of hydrogen liberated from a voltameter (nickel electrodes in a solution of sodium hydroxide) in series with the electrolytic cell. In these experiments, it was, of course, necessary to use a divided cell, each cathode being contained in a porous pot. The apparatus used was similar to that described by Müller and Schellhaas (*Zeitsch. Elektrochem.*, 1907, **13**, 257).

An abstract of the results obtained is given in the following tables. The solutions contained one gram of sodium benzyl thiosulphate and one equivalent of sodium carbonate in 40 c.c. The times given are expressed in percentages of the theoretical time necessary for complete reduction. The "per cent. H" signifies the percentage of hydrogen used in reduction.

C.D. = 1·03.		C.D. = 0·685.		C.D. = 0·125.	
Time.	Per cent. H.	Time.	Per cent. H.	Time.	Per cent. H.
7·7	38·8	15·4	57·8	1·4	97·3
30·8	38·6	46·1	48·7	11·2	85·3
53·8	(41·1)	76·9	43·7	19·7	81·8
76·9	37·7	100·0	40·1	28·1	78·3
100·0	31·7	130·8	30·7	36·5	77·7
123·1	24·8	161·5	23·7	44·9	73·1
146·2	19·0	192·3	13·5	53·4	73·9
169·2	12·1	223·2	13·2	61·8	70·4

A lower current density thus increases the percentage of hydrogen used in reduction. Of the following tables, the first shows that a lead cathode gives slightly better results than one of platinum, the strength of solution being the same as above. The second table shows that an increase in concentration of the solution also gives better results; the solution contained 4 grams of sodium benzyl thiosulphate and the equivalent quantity of sodium carbonate in 40 c.c. of water.

C.D. = 0·125.		C.D. = 0·685.	
Time.	Per cent. H.	Time.	Per cent. H.
1·4	100·0	1·9	81·4
9·8	100·0	9·6	80·4
18·3	88·7	17·4	77·2
26·7	89·7	25·1	72·3
35·1	89·6	32·8	68·7
43·5	81·3	40·5	66·8
52·0	79·7	48·3	64·5
60·4	77·7	56·0	59·2

The crude disulphide obtained with the lead cathode was somewhat discoloured, but one recrystallisation from alcohol gave the pure product. Other experiments showed that the addition of a larger excess of sodium carbonate (for example, 5 equivalents) had a retarding effect on the reduction.

A few experiments have been made in which the electrolyte was vigorously stirred (the cathode was stationary). The results given in the following table show that the percentage of hydrogen consumed in reduction decreases slowly at first, since the effect of stirring is continuously to supply fresh portions of the electrolyte to the cathode, but after a time, when most of the compound has been reduced, the percentage of hydrogen used falls rapidly. Only one set of results is given, since indications have been obtained that the previous treatment of the cathode (platinum) must be taken into account, and so far we have not investigated this. The solution contained one gram of sodium benzyl thiosulphate and one equivalent of sodium carbonate in 40 c.c. C.D. = 2.

Time.	Per cent. H.	Time.	Per cent. H.
5·6	30·9	123·6	30·9
39·3	38·1	174·2	26·0
56·2	39·1	207·9	13·1
73·0	34·0	241·6	8·5
89·9	34·3	269·6	3·7

Electrolysis without Isolating the Sodium Benzyl Thiosulphate.

As pointed out in the introduction, it was necessary to use a divided cell. In the first experiments, the electrodes were stationary. The method of procedure was as follows. Five grams of benzyl chloride and 20 c.c. of 90 per cent. alcohol were added to a solution of 12 grams of sodium thiosulphate in 20 c.c. of water, and the mixture heated on the water-bath under a reflux condenser for one to one and a half hours. When cold, two equivalents of sodium carbonate* (11·5 grams) dissolved in 30 c.c. of water were added, and the solution was filtered from the turbidity which formed. The liquid was then electrolysed, using a platinum cathode, the anode, either of nickel or platinum, being enclosed in a porous pot or in a parchment tube which contained a strong solution of sodium carbonate. The yields obtained were as follows:

Current, per cent.	C.D.	Temp.	Yield, per cent.
111·7	1·27	Room temp.	53·5
97·8	1·27	,, ,,	59·7
159·4	1·40	,, ,,	86·4
111·8	2·54	60—70°	82·3
98·8	1·27	60—70	80·0

The hot solutions thus gave the best yields. The product from the cold solutions was purer, possessing only a faint pink tinge, whilst that from the hot solution had a deeper colour. In both cases, one recrystallisation gave the pure product.

In the next experiments, the cathode was rotated during the electrolysis, the anode being in the outer chamber. The inner chamber consisted of a wide glass tube, over the bottom end of which some parchment was securely fastened. The theoretical current as indicated by the ammeter—measurements were not made with a coulometer in circuit—was passed in each case, the current density being 1·2 amperes per square dcm. The temperature was that of the room.

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* With a divided cell, it is not necessary to add the sodium carbonate to the solution at the cathode, but it is advisable, since the CO_3''- and OH'-ions will carry most of the current and thus prevent the complex ion $C_6H_5{\cdot}CH_2{\cdot}S_2O_3'$ from being carried to the anode.

Experiment 1.—The solution was not filtered after the addition of the solution of sodium carbonate. The crude product was white, and the yield 86·4 per cent.

Experiment 2.—No solution of sodium carbonate was added. The crude product was white, and the yield 79·4 per cent.

Thus a rotating cathode improves the yield, and the addition of sodium carbonate, although not necessary, is advisable.

The pure *dibenzyl disulphide* melted at 71°:

0·2222 gave 0·4186 $BaSO_4$. S = 25·87.

$(C_6H_5 \cdot CH_2)_2S_2$ requires S = 26·02 per cent.

The *compound* with silver nitrate gave Ag = 26·0;

$(C_7H_7)_2S_2, AgNO_3$ requires Ag = 26·0 per cent.

Preparation of Diethyl Disulphide.

(1) Ten grams of sodium ethyl thiosulphate were dissolved in 20 c.c. of water and 4 grams of sodium bicarbonate, dissolved in the minimum amount of water, added. The solution was electrolysed in a beaker with a platinum wire anode and cathode of platinum foil, 1·4—1·5 amperes (C.D = 4, approx.) being passed for one and a half hours. The oil (diethyl disulphide) which floated on the surface of the liquid was then separated, and the current again passed through the aqueous solution; no more disulphide was formed. The disulphide was then extracted with ether, and the ethereal solution dried over calcium chloride. After removing the ether, a pale yellow liquid was left, which weighed 2·2 grams (a yield of 58 per cent.). On distillation, nearly all the liquid passed over at 152°; the distillate was colourless, and had all the properties of *diethyl disulphide*.

(2) Twenty grams of sodium thiosulphate were dissolved in 40 c.c. of water and 10 grams of ethyl iodide, and 40 c.c. of 90 per cent. alcohol added. The mixture was heated on the water-bath for one and a half hours, when a homogeneous solution was obtained. 18·5 Grams of sodium carbonate, dissolved in 40 c.c. of water, were then added to the cold solution, and the mixture electrolysed in a divided cell, using a rotating cathode. The current density was 1 ampere per sq. dcm., and five-fourths of the theoretical current was passed. The oil which separated was treated as in (1), and the distillate obtained weighed 1·7 grams (yield = 43 per cent.):

0·2232 gave 0·8436 $BaSO_4$. S = 51·9.

$(C_2H_5)_2S_2$ requires S = 52·5 per cent.

0·1763 of the *compound* with silver nitrate gave 0·0651 Ag. Ag = 36·9.

$(C_2H_5)_2S_2, AgNO_3$ requires Ag = 36·9 per cent.

Part of the expense of the foregoing investigations was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks. The research is being continued in various directions.

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CXCVIII.—*The Double Nitrites of Mercury and the Alkali Metals.*

By Prafulla Chandra Rây.

On several occasions I have shown that when mercurous nitrite is treated with a large volume of water, it undergoes dissociation in accordance with the equation: $Hg_2(NO_2)_2 = Hg + Hg(NO_2)_2$, and that nearly 22 per cent. of the salt remains in solution as such, further dilution having no effect (*Zeitsch. anorg. Chem.*, 1896, **12**, 372; Trans., 1897, **71**, 340).

In a paper communicated to the Society about eight years ago I also pointed out that if a sufficient excess of potassium or sodium nitrite or even of silver nitrite is added to this solution, the unchanged portion of mercurous nitrite at once breaks up as above, whilst the alkali nitrite remains unaffected (Proc., 1899, **15**, 103). I was at that time unable to account for this anomalous behaviour.

My more recent work, however, has furnished an explanation. The further dissociation of mercurous nitrite ceases as soon as a rather stable compound, mercuroso-mercuric nitrite, $(HgNO_2)_2 + 4Hg(NO_2)_2$, is formed (Trans., 1902, **81**, 645), and if to this solution an alkali nitrite is added, the latter at once enters into combination with mercuric nitrite, a more stable compound being formed. The mercurous nitrite thus displaced, not being stable by itself in presence of water, at once dissociates; and this process is further accelerated because of the tendency of one of the products of dissociation, namely, mercuric nitrite, to unite with the alkali nitrite. A new method has thus been furnished for the preparation of a series of double salts.

General Method of Preparation.—A mixture of mercurous and alkali nitrite is rubbed to a paste with a minimum quantity of water, more water is gradually added, and the undissolved portion filtered off. On evaporating the filtrate, which is of a pale yellow colour, over sulphuric acid under diminished pressure, pale yellow, glistening tablets and prisms are obtained, which are invariably readily soluble in water. It should be noted here that Lang (*J. pr. Chem.*, 1862, **86**, 295) and Rosenheim and Oppenheim (*Zeitsch. anorg. Chem.*, 1901, **28**, 171) have already prepared some of the compounds described below by treating mercuric nitrate with concentrated solutions of potassium and sodium nitrites and evaporating the filtrate.

I. *Mercuric Potassium Nitrites.*

I have succeeded in preparing two salts of the formula $Hg(NO_2)_2 + 2KNO_2$ and $Hg(NO_2)_2 + 3KNO_2 + H_2O$ respectively. As will be shown below, mercuric nitrite combines with one, two, three, and even four molecules of the alkali nitrites, the actual number depending on the excess of the latter.

(*a*) $Hg(NO_2)_3 + 2KNO_2$. Analysis gave:

Found (1) Hg = 41·24 ; K = 16·99 ; N = 12·16.
,, (2) Hg = 40·99* ; K = 17·38.

Theory requires:

Hg = 43·26 ; K = 16·92 ; N = 12·12 per cent.

From the mother-liquor of this salt, Rosenheim and Oppenheim have prepared another salt of the formula $Hg(NO_2)_2 + KNO_2$.

(*b*) $Hg(NO_2)_2 + 3KNO_2 + H_2O$. Analysis gave:

Hg = 35·19 ; K = 20·24 ; N = 12·00.

Theory requires:

Hg = 35·38 ; K = 20·75 ; N = 12·38 per cent.

The peculiarity of this salt is that, although hydrated, it does not give up its water, but retains its lustre intact when kept in a vacuum desiccator over sulphuric acid. Kohlschütter, who has also examined this compound, found that it does not lose water when heated at 100° for a long time (*Ber.*, 1902, **35**, 489).

II. *Mercuric Sodium Nitrites.*

(*a*) $Hg(NO_2)_2 + 1\frac{1}{2}NaNO_2$. Analysis gave:

Hg = 50·12 ; Na = 12·87 ; N = 8·43.

Theory requires:

Hg = 50·57 ; Na = 12·39 ; N = 8·72 per cent.

This compound has not been described by previous workers in this field.

(*b*) $Hg(NO_2)_2 + 2NaNO_2 + 2H_2O$. Analysis gave:

Hg = 43·15 ; Na = 10·40 ; N = 11·76 ; H_2O† = 7·62.

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* The unusually low percentage of mercury is probably due to the salt being contaminated with traces of (*b*).

† The water was estimated by the direct method.

Theory requires :

$Hg = 42·92$; $Na = 9·87$; $N = 12·02$; $H_2O = 7·73$ per cent.

This salt is deliquescent.

Rosenheim and Oppenheim, as also Kohlschütter (*loc. cit.*), describe only the anhydrous variety of this compound, which I have not succeeded in preparing. The analysis given above is that of glistening, small prisms, which did not diminish in lustre even in a vacuum desiccator. The non-efflorescence of this and of the hydrated potassium salt indicate that the water is not loosely combined.

III. *Mercuric Lithium Nitrites.*

$Hg(NO_2)_2 + 4LiNO_2 + 4H_2O$ Analysis gave :

Found (1) $Hg = 36·15$; $Li = 4·68$.
„ (2) $Hg = 34·95$; $Li = 4·76$; $N = 15·08$.

Theory requires :

$Hg = 34·72$; $Li = 4·87$; $N = 14·58$ per cent.

This salt was obtained as a crystalline mass and is, like other lithium compounds, extremely deliquescent.

From the mother-liquor of the above, a salt of the composition $Hg(NO_2)_2 + LiNO_2 + H_2O$ crystallised out. Analysis gave :

$Hg = 48·50$; $Li = 2·89$; $N = 13·15$.

Theory requires :

$Hg = 48·02$; $Li = 3·37$; $N = 13·46$ per cent.

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CXCIX.—*Silver-mercuroso-mercuric Oxynitrates and the Isomorphous Replacement of Univalent Mercury by Silver.*

By Prafulla Chandra Rây.

I have already shown that the action of silver nitrite on a solution of mercuroso-mercuric nitrite is similar to that of the alkali nitrites with the addition that, not only is mercury separated, but metallic silver is also deposited in shining, minute crystals. There is, however, no evolution of nitrogen nor any change in the radicle NO_2 (Proc., 1899, **15**, 103).

Owing to the sparing solubility of silver nitrite, my former experiments were made with boiling solutions. Now, however, the conditions have been somewhat modified. Mercurous and silver nitrites are rubbed to a fine paste with the minimum quantity of water, dilution with more water being then effected gradually, and the pale yellow filtrate evaporated under diminished pressure over sulphuric acid. By this procedure, it was expected that a double salt of the type described in the preceding paper would be formed in which the place of the alkali nitrite would be taken by silver nitrite; but lemon-yellow, crystalline products resulted containing both mercurous and mercuric mercury, as well as silver, and the acid radicle was *nitrate* instead of nitrite.

Although mercuroso-mercuric nitrite is quite stable in solution, it cannot be isolated in the solid state, for when the solution is concentrated by spontaneous evaporation mercuroso-mercuric oxynitrates crystallise out in succession (Trans., 1905, **87**, 174). In the present instance, as the reaction takes place in the cold, only a small proportion of mercurous nitrite is replaced by silver nitrite, owing to its slight solubility, and the solution thus contains a mixture of silver mercuric nitrite and mercuroso-mercuric nitrite. During the process of concentration two reactions evidently proceed side by side:

$$3Hg_2(NO_2)_2 = 4NO + 3Hg_2O\cdot N_2O_5.$$
$$3Hg(NO_2)_2 = 4NO + 3HgO\cdot N_2O_5.^*$$

Thus, although silver nitrite is a stable salt and can be crystallised without undergoing decomposition, it is here slowly converted into nitrate owing to the formation of nitric acid. Had there been no silver salt present, the first crop of crystals would have consisted of α-oxymercurosic nitrate, $HgO\cdot 2Hg_2O\cdot N_2O_5$. A salt of this type was, indeed, formed amongst others, but, as will be shown below, a portion of mercurous mercury was in each case replaced by its equivalent of silver. It is to be regretted that as the salts were of a microcrystalline form, they could not be examined crystallographically.

Method of Analysis.—The finely-powdered substance was dissolved in the minimum quantity of cold dilute nitric acid. Silver and mercurous mercury were precipitated by the addition of pure sodium chloride, the mercuric mercury remaining in solution. The precipitate, after careful washing with water, was treated with hydrochloric acid and one or two crystals of potassium chlorate and gently warmed, the solution being then largely diluted with water and set aside to allow the silver chloride to subside. The filtrate now represented mercurous mercury, although, of course, oxidised to the mercuric state. Analysis of two different preparations of this typical salt are given below.

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[*] And possibly also according to the equation $Hg(NO_2)_2 = HgNO_3 + NO$ (Trans. 1904, **85**, 527).

Owing to the fact that mercurous chloride is appreciably soluble in sodium chloride, the mercuric mercury often appears slightly higher:

	Found.	
	Preparation I.	Preparation II.
Mercurous mercury (Hg′)	57·80	54·83
Silver	6·13	6·77
Mercuric mercury (Hg″)	19·50	17·85
Nitrogen	2·85	--

The ratio (Hg′·Ag) : Hg″ : N in I is approximately 4 : 1 : 2.
,, (Hg′·Ag) : Hg″ in II is 4 : 1.

It should be understood that the ratio of the metals is not invariably as 4 : 1, as is shown by the analyses of two successive crops of another preparation:

	Found.		
	Preparation III.		
	1st crop.	2nd crop.	Preparation IV.
Hg′	58·98	45·81	48·04
Ag	7·92	4·15	3·79
Hg″...............	10·47	26·23	30·67
N..................	5·80	4·04	3·60

The ratios (Hg′·Ag) : Hg″ : N are respectively 7 : 1 : 8, 2 : 1 : 2, 1·8 : 1 : 1·7.

Judging from the distribution of the base and acid, it will be seen that preparations I and II are the most basic, and preparation III the least, whilst that represented by the second crop of preparation III stands intermediate between the two.

Discussion of Results.

The silver and mercurous nitrites were not weighed out in fixed proportions, but simply dissolved together by trituration in a mortar with cold water; hence at the start the components in solution often varied within wide limits. As a result of an extensive investigation on the "conjugated sulphates of the copper-magnesium group" (*Proc. Roy. Soc. Edin.*, 1888, **15**, 267), it was proved by the author that if the components are dissolved in equivalent proportions and successive crops collected at intervals, the crystals contain the component sulphates in definite proportions. Thus in the case of copper cobalt potassium sulphate two successive crops had Cu : Co = 5 : 4, whilst in the third crop the ratio was at 1 : 1 (*loc. cit.*, p. 275). In the case of iron zinc ammonium sulphate, the first three fractions had the same composition with the ratio of Fe : Zn = 1 : 3; the next three fractions had also identical composition, only the ratio of the two metals was as 2 : 5. In short, it was established that the change in composition between two "crops" was not in any sense *continuous*, but distinctly *abrupt* (*loc. cit.*, p. 281).

In the present instance, it is also evident that within fairly wide limits in the distribution of the components in solution the ratio of $Hg'' : (Hg'\cdot Ag) = 1 : 4$, and that in successive crops the change in the ratio of the metals is abrupt and not in slow gradations. Thus, in preparation III, whilst the first crop had $Hg'' : (Hg'\cdot Ag) = 1 : 7$, the ratio in the second was as 1 : 2. In preparation IV, the first crop which was analysed had the ratio of $Hg'' : (Hg'\cdot Ag) = 1 : 1{\cdot}8$ instead of 1 : 2; it will be seen that it approached in composition the second crop of preparation III. This apparent anomaly appears to be due to the fact that a salt was actually formed in which $Hg'' : (Hg'\cdot Ag) : N = 1 : 2 : 2$; but owing to delay in collecting it another salt richer in mercuric mercury had already begun to be deposited. In other words, this is a case of overlapping of two consecutive crops.

It is, of course, well known that in the case of a solution containing isomorphous mixtures the ordinary laws of solubility hold good—the first crop being rich in the least soluble constituent; but as the latter is to a large extent fractionally removed from the field by the first and second crystallisations, the conditions begin to alter in the reverse direction, the mother-liquor gradually becoming richer in the more soluble constituent, and this is no doubt the reason why in the second crop of preparation III the proportion of mercurous mercury and silver $(Hg'\cdot Ag)$ diminished. Although in the present series of oxynitrates the ratio between Hg'' and $(Hg'\cdot Ag)$ appears in simple integers, the criterion of isomorphism is equally satisfied. Thus in both the preparations I and II, while the ratio of $Hg'' : (Hg'\cdot Ag)$ remains constant, the percentage of the different metals varies.[*]

A few words on the position of univalent mercury in the periodic system may not be out of place here. Throughout the investigation on mercurous nitrite and hyponitrite, which has been going on during the last twelve years, very marked and striking similarity in properties has been found to obtain between these compounds and their silver analogues (compare Trans., 1897, **71**, 350; *Annalen,* 1901, **316**, 253; Proc., 1907, **23**, 89). The isomorphous replacement of univalent mercury by silver still further emphasises this family likeness. The univalent metals, copper, silver, and gold, have been placed in the first group surrounded by brackets as members of the odd series. Copper and silver isomorphously replace each other in a number of native sulphur compounds as also in the complicated triple thiocyanates.[†] But the relationship of these two metals with gold is at best very remote. In view of the evidence now adduced, it would appear more rational to substitute mercury for gold and relegate the latter to its more congenial place in the eighth group immediately after platinum. Univalent mercury should be regarded as quite a distinct metal from bivalent mercury; the former is related by ties of closest affinity to silver, whilst the latter is related to members of the second group, namely, magnesium and zinc.*

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[*] Compare "Haben die isomorphen Körper die Fähigkeit, miteinander krystallisirbare Mischungen zu bilden, in welchen die Mengen der Bestandtheile in einem irrationalen Verhaltniss zu einander stehen. Diese Eigenschaft bietet zugleich auch das beste. ja einzige Kriterium für die Isomorphie."—Dr. Arzruni in *Neu Handwörterbuch d. Chem.*, Article: "Isomorphie."

[†] Groth's "Chemical Crystallography," trans. by Marshall, p. 73.

From the foregoing investigation, it follows that when a solution containing mercuroso-mercuric nitrite and silver mercuric nitrite is allowed to evaporate spontaneously, a series of hydrated silver-mercuroso-mercuric oxynitrates crystallises out, in each of which mercurous mercury is isomorphously replaced by silver. It is worthy of note that the present series of compounds are all basic and hydrated.† They retain their lustre untarnished, and do not lose water over sulphuric acid in a vacuum; they give up water, however, readily when heated. It would appear that the predominant partner, univalent mercury, impresses its own characteristics upon silver, for silver as a rule does not form basic or hydrated salts (compare Rây, *Zeitsch. anorg. Chem.*, 1896, **12**, 374).

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CC.—*The Constituents of the Essential Oil of Nutmeg.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

ALTHOUGH the essential oil distilled from the nutmeg has been known for more than three centuries, and, being recognised by several national Pharmacopœias, has long been an established article of commerce, it is a remarkable fact that up to the present time very little of a definite character has been ascertained respecting the nature of its constituents. The previous investigations pertaining to this subject have been recorded by Gildemeister and Hoffmann in their work entitled "Die ætherischen Oele," Berlin, 1899, p. 474, and also by Semmler in his more recent work, "Die ætherischen Oele," Leipzig, 1906, Bd. I, p. 768; II, 314; III, 211; IV, 165. The correct interpretation of the results of the earlier investigations is, however, rendered somewhat difficult by the fact that the essential oil of nutmeg has frequently been designated as oil of mace (compare *Pharmacopœia Germanica*, 4th Edition, p. 269), and that the source or genuineness of the oil employed has not always been clearly indicated. It is, indeed, generally assumed that the oils of nutmeg and mace are qualitatively identical, and that they differ only in the relative proportions of their constituents, but, inasmuch as neither of these oils has hitherto been completely examined, there is no direct evidence that this is the case.

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* On the twofold position of mercury in the periodic system. See also Trans., 1905, **87**, 189. In this respect, mercury is comparable to thallium, which with variation of valency affords a remarkable instance of variation of chemical character.

† The researches of Súlc and recently of Watson have also conclusively proved the existence of silver peroxynitrates (Trans., 1906, **89**, 578).

Among the more important of the earlier investigations of oil of nutmeg, those of Gladstone may be considered. In his first communication on this subject (*Journ. Chem. Soc.*, 1864, **17**, 11), he recorded the following observations. "The three specimens examined consisted of varying proportions of a hydrocarbon resembling carvene, and an oxidised oil with the boiling point 224°, and sp. gr. 0·9466. As it closely resembles carvol and menthol in its properties, it may by analogy be named myristicol." In a later communication (*Journ. Chem. Soc.*, 1872, **25**, 3, 11), Gladstone suggested for the above-mentioned hydrocarbon the name "myristicene," and remarked further regarding "myristicol" as follows: "This oil has the characteristic smell of nutmeg, and . . . does not form a crystalline compound with hydrosulphuric acid. It was found difficult to purify it by fractional distillation, indeed there was some reason to think that in the process of rectification it was subject to change. An ultimate analysis of portions boiling at somewhere about 220° yielded rather too much carbon and hydrogen for the formula $C_{10}H_{14}O$, suggesting the idea of its being still mixed with some amount of a hydrocarbon."

The constituents of nutmeg oil were next investigated by C. R. A. Wright (*Journ. Chem. Soc.*, 1873, **26**, 549), who obtained "a considerable quantity of a mixture of hydrocarbons boiling below 180° and a small quantity of an oxidised constituent boiling above 210°, apparently the 'myristicol' of Gladstone." He noted that the purest myristicol boiled at 212—218°, and from an analysis of this fraction concluded that it contained as its principal constituent a body isomeric with camphor, $C_{10}H_{16}O$, but as he obtained from it, by repeated distillation, a portion boiling at 250—265°, which was assumed to be a polymerised product, the conclusion respecting the composition of the fraction was evidently not justified. With regard to the hydrocarbons, Wright stated that, "contrary to Gladstone's experiments, the hydrocarbon of oil of nutmeg is not a single body boiling at 167° and of formula $C_{10}H_{16}$, but a mixture of a terpene boiling at 163—164° and a hydrocarbon, apparently cymene, boiling towards 177°." As the cymene, however, was only isolated after treating the mixture with sulphuric acid, no evidence was afforded of its pre-existence in the oil.

Brühl (*Ber.*, 1888, **21**, 472), with consideration of the statements respecting the character of the so-called "myristicol," and from purely physical data, which apparently were obtained by the examination of a fraction of nutmeg oil boiling at 224°, was led to the conclusion that, as an alcohol of the formula $C_{10}H_{16}O$, myristicol was to be regarded as a cyclic compound containing two ethylenic linkings. He, moreover, suggested constitutional formulæ which were believed to be in accordance with the physical determinations.

Wallach (*Annalen*, 1889, **252**, 105) examined the lower boiling portions of an oil which he designated as "mace oil," and positively established the presence of pinene and dipentene. In this connexion, he noted that "it was remarkable that the fractions containing pinene were nearly inactive (very slightly lævorotatory). The crude oil, on the other hand, as also the fractions of higher boiling point, were strongly dextrorotatory. It is to be assumed that in the low boiling portion, + and − pinene neutralise each other. The nature of the higher boiling, dextrorotatory portions of mace oil still remains to be cleared up."

The investigation of the oils of nutmeg and mace was subsequently undertaken by Semmler (*Ber.*, 1890, **23**, 1803; 1891, **24**, 3818). The oil of nutmeg supplied to him had a density of 0·8611 at 15°, and was found to consist entirely of terpenes, but these were not further examined. He particularly noted the absence of cymene, "myristicol," and higher boiling oils of high specific gravity, and stated that the oil in question evidently represented the portions which are most volatile in steam. These results led Semmler to examine an oil of mace, which was found to have a specific gravity of 0·9309 at 14°, and to give a green coloration with ferric chloride, indicating the presence of a phenolic substance. A fraction collected between 70° and 144° at 10 mm. pressure was assumed to contain "myristicol," but was not further examined. From the higher boiling portions of the oil, after treatment with sodium, a crystalline substance was isolated, to which Semmler gave the name myristicin, and assigned to it the formula $C_{12}H_{14}O_3$. It was subsequently shown, however, that myristicin has the formula $C_{11}H_{12}O_3$, and is 3-methoxy-4 : 5-methylenedioxy-1-allylbenzene. This substance is a liquid, but, by treatment with metallic sodium or with alkalis, it is readily converted into the corresponding propenyl compound (m. p. 45°), which has been designated *iso*myristicin (compare Thoms, *Ber.*, 1903, **36**, 3446; Richter, *Ber. Deut. pharm. Ges.*, 1907, **17**, 152; Rimini, *Gazzetta*, **34**, ii, 281; **35**, i, 406; Rimini and Olivari, *Atti R. Accad. Lincei*, 1907, [v], **16**, i, 663).

The purpose of the present investigation has been to ascertain the nature of the constituents of a genuine oil of nutmeg, and especially, among other points of interest, to determine the character of the so-called "myristicol." In addition to the statements (*loc. cit.*) regarding the occurrence of this compound in oil of nutmeg, Wright (*Journ. Chem. Soc.*, 1873, **26**, 552) believed it to be also present in very small amount in the oil of sweet orange. He noted that "the portion passing over at 210—230° appeared to be identical with myristicol, as it gave numbers agreeing with the formula $C_{10}H_{16}O$." Quite recently, Thoms (*Ber. Deut. pharm. Ges.*, 1904, **14**, 27) has indicated that the essential oil distilled from the seed of *Monodora Myristica*, Dunal, contains an oxygenated compound of the composition $C_{10}H_{16}O$, which he regarded as probably identical with "myristicol." In connexion with these later observations, it is, however, of interest to note that the constituent of oil of sweet orange which Wright had considered to be identical with "myristicol" has been shown by Stephan (*J. pr. Chem.*, 1900, [ii], **62**, 531) to be nothing more than *d*-terpineol.

EXPERIMENTAL.

I. *Examination of a Normal Oil of Nutmeg.*

The oil employed in this investigation was specially distilled for us by Messrs. Stafford Allen & Sons, of London, from unlimed Ceylon nutmegs of good quality, and our thanks are due to them for the care with which the operation was conducted. The amount of oil obtained from 24·38 kilograms of nutmegs was 1693 grams, corresponding to a yield of 6·94 per cent. This oil was a nearly colourless, limpid liquid, having a density of 0·8690 at 15°/15°, an optical rotation of +38°4′ in a 1-dcm. tube, and was soluble in three times its volume of 90 per cent. alcohol.

A determination of the amount of free acids and esters gave the following data: 20 grams of the oil required 2·9 c.c. of an *N*/10 alcoholic solution of potassium hydroxide to neutralise the free acids, corresponding to an acid value of 0·81. On subsequently adding an excess of the alkali and boiling for half an hour, it was found that 11·2 c.c. of the decinormal solution were required to hydrolyse the esters present, corresponding to an ester value of 3·15. The esters, if calculated as $C_{10}H_{17}\cdot C_2H_3O_2$, would therefore amount to 1·1 per cent.

As a preliminary test for the presence of aldehydes or ketones, 20 grams of the oil were shaken for some time with a saturated solution of sodium bisulphite. No solid compound was formed, but the aqueous liquid, after being freed from adhering oil by shaking with ether, gave on treatment with alkali a trace of an oil which possessed a fragrant odour. The amount of this substance was, however, much too small to permit of its isolation.

Treatment with Sodium Hydroxide.—A quantity (1500 grams) of the oil was extracted several times with a 5 per cent. solution of sodium hydroxide, in order to remove the free acids and any phenolic substances present. The combined alkaline liquids and aqueous washings were shaken with ether to remove any adhering oil, and then acidified with sulphuric acid, when an oily liquid separated. This was extracted with ether, and the ethereal liquid shaken a few times with a 10 per cent. solution of sodium carbonate.

Identification of Myristic Acid.

The liquids resulting from the extraction with sodium carbonate were acidified with sulphuric acid and distilled with steam. The distillate contained no volatile acids, but there remained in the flask a quantity of a solid substance amounting to about 5 grams, which was collected on a filter and washed with water. On crystallisation from alcohol, it yielded a product melting sharply at 54°:

0·1482 gave 0·3990 CO_2 and 0·1690 H_2O. C = 73·4 ; H = 12·7.

$C_{14}H_{28}O_2$ requires C = 73·7 ; H = 12·3 per cent.

This substance was thus identified as myristic acid.

Identification of Eugenol and iso*Eugenol.*

The ethereal liquid which had been extracted with a solution of sodium carbonate, as above described, was dried with anhydrous sodium sulphate, and the ether removed. About 3 grams of a dark brown oil were thus obtained, which possessed an intense odour of eugenol and gave with ferric chloride a deep green colour. By distillation under a pressure of 75 mm., it was resolved into the following three fractions: 164—174° ; 174—180°; above 180°/75 mm., only a little non-volatile, resinous substance remaining in the flask. These products were then separately benzoylated, when from the first fraction (b. p. 164—174°/75 mm.) a benzoyl derivative was obtained, which, after fractional crystallisation from alcohol, separated in thick prisms, melting at 67—69°:

0·1705 gave 0·4760 CO_2 and 0·0955 H_2O. C = 76·1 ; H = 6·2.

$C_{17}H_{16}O_3$ requires C = 76·1 ; H = 6·0 per cent.

The substance yielding this compound was thus identified as eugenol.

The second fraction (b. p. 174—180°/75 mm.) yielded a mixture of benzoyl derivatives, for, when crystallised from alcohol, the first crop of crystals melted somewhat indefinitely between 68° and 84°. After repeated fractional crystallisation, this product melted at 96—100°, and was then analysed:

0·1500 gave 0·4158 CO_2 and 0·0851 H_2O. C = 75·6; H = 6·3.
0·1385 „ 0·3862 CO_2 „ 0·0776 H_2O. C = 76·0; H = 6·2.
$C_{17}H_{16}O_3$ requires C = 76·1; H = 6·0 per cent.

From the melting point and analysis of this compound, it is evident that it was nearly pure benzoyl*iso*eugenol, which is stated to melt at 103—104°. The identification of *iso*eugenol as a constituent of nutmeg oil is of considerable interest, inasmuch as hitherto but one instance appears to have been recorded of its occurrence in an essential oil (compare Semmler, "Die ætherischen Oele," Bd. IV, p. 130). The fraction of the phenols boiling above 180°/75 mm. yielded no solid benzoyl derivative.

Preliminary Examination of the Terpenes.

The oil from which the myristic acid and phenols had been removed, as above described, was washed with water, dried with anhydrous sodium sulphate, and distilled under a pressure of 60 mm. The portion boiling below 110°/60 mm., which would contain practically all the terpenes, was separately collected, and amounted to about 87 per cent. of the entire oil. This portion was subsequently subjected to several fractionations under a pressure of 20 mm., and a fraction boiling below 70°/20 mm. was collected. The density of the latter was found to be 0·8526 at 15°/15°, which proved the absence of any appreciable amount of an olefinic terpene. A portion of the oil which distilled at 170—172° under the ordinary pressure was specially tested for phellandrene, but with a negative result. The further examination of the terpenes was conducted after the hydrolysis of the higher boiling portions of the oil.

Hydrolysis of the Oil.

The portion of oil collected below 110°/60 mm., as also that boiling above this temperature, was distilled under the ordinary pressure, and the fraction passing over below 190° was collected.

The entire amount of oil boiling above 190° under the ordinary pressure was heated for an hour with an alcoholic solution of 10 grams of potassium hydroxide in a flask provided with a reflux condenser. After distilling off the greater part of the alcohol, water was added, and the mixture extracted with ether. The ethereal liquid was washed, dried, and the ether removed, after which the hydrolysed oil was distilled under 15 mm. pressure in order to remove any non-volatile, resinous matter. The strongly alkaline, aqueous liquid, which remained in the flask after the extraction of the hydrolysed oil, was reserved for the examination of the acids.

Fractional Distillation of the Oil.

The hydrolysed oil, together with the portion boiling below 190°, which had previously been separated, was next submitted to a systematic fractional distillation at the ordinary pressure, a Young's rod and disc column having been used up to a temperature of 205°. The following fractions were ultimately obtained :

Boiling-point.	$d\ 20°/20°$.	α_D in a 1 dcm. tube.	Amount in grams.
156—159°	0·8519	+31° 36′	136·0
159—161	0·8513	+45 15	351·0
161—163	0·8515	+52 10	229·0
163—165	0·8516	+48 48	135·0
165—170	0·8514	+35 46	29·0
170—180	0·8521	+ 9 1	77·0
180—195	0·8754	+ 4 21	22·0
195—205	0·9149	+10 40	9·2
205—215	0·9351	+12 44	19·5
215—225	0·9504	+ 9 12	18·0
225—235	0·9656	+ 5 24	8·1
235—245	0·9812	+ 4 12	6·8
245—255	0·9931	+ 5 20	10·2
255—265	1·0166	+ 5 20	17·1
265—275	1·0436	+ 5 40	24·2
Above 275	1·0510	+ 2 25	5·0
		Total ...	1097·1 grams.

Identification of Pinene.

Fraction 156—159°.—This was a colourless, limpid liquid, which possessed the odour of pinene :

0·1018 gave 0·3282 CO_2 and 0·1100 H_2O. C = 87·9 ; H = 12·0.

$C_{10}H_{16}$ requires C = 88·2 ; H = 11·8 per cent.

It is evident that this fraction consisted entirely of a hydrocarbon. The presence of pinene was determined by the formation of a crystalline nitrosochloride (m. p. 108°), and the conversion of the latter into the corresponding nitrolbenzylamine (m. p. 123°).

Fraction 159—161°.—This was the largest fraction obtained, and it resembled in its characters the preceding one :

0·0958 gave 0·3100 CO_2 and 0·1034 H_2O. C = 88·3 ; H = 12·0.

$C_{10}H_{16}$ requires C = 88·2 ; H = 11·8 per cent.

It was found to contain a considerable quantity of pinene, since it readily yielded the above-mentioned derivatives of this terpene.

Identification of Camphene.

Fraction 161—163°.—This was a large fraction, and resembled in odour the preceding one:

0·1441 gave 0·4650 CO_2 and 0·1555 H_2O. C = 88·0; H = 12·0.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

The high optical rotation of this fraction suggested the presence of a considerable amount of camphene. Fifty grams of the liquid were therefore treated with a mixture of acetic and sulphuric acids according to the method of Bertram and Walbaum for the conversion of camphene into an *iso*borneol ester. After hydrolysing the product, a pale yellow oil was obtained, which was distilled under diminished pressure. A portion which passed over at 120—140°/25 mm. partially solidified in the receiver, and possessed a pronounced camphoraceous odour. On treating this fraction with phenyl*iso*cyanate in a sealed tube at 100° for several hours, a phenylurethane was obtained, which crystallised from alcohol in fine needles melting at 138°. The latter compound, on treatment with alcoholic potash, yielded a substance which, after crystallising from methyl alcohol, melted at 207—212°, and had all the characteristic properties of *iso*borneol. The presence of camphene in this fraction of the oil was thus established.

Fractions 163—165° and 165—170°.—These fractions were similar in their general characters to the preceding one, but had a somewhat lower rotatory power. The fraction 165—170° was analysed:

0·1062 gave 0·3430 CO_2 and 0·1150 H_2O. C = 88·1; H = 12·0.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

It was evident that these two fractions consisted of mixtures of pinene and camphene with the constituents of the succeeding fraction.

Identification of Dipentene.

Fraction 170—180°.—This was a limpid, colourless liquid, possessing a distinctly lemon-like odour:

0·1171 gave 0·3778 CO_2 and 0·1244 H_2O. C = 88·0; H = 11·8.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

The analysis of this fraction showed that it contained no oxygenated substances, such as cineol (b. p. 176°). The fraction readily yielded a bromo-derivative, which, after crystallisation from ethyl acetate, melted at 124—125°, thus establishing the presence of dipentene. No terpinene could be detected in it.

Fraction 180—195°.—This was a colourless liquid, possessing a somewhat lemon-like odour:

0·1567 gave 0·4867 CO_2 and 0·1650 H_2O. C = 84·7; H = 11·7.

The characters of this fraction indicated it to consist of a mixture of the constituents of the preceding and succeeding ones.

Identification of Linalool.

Fraction 195—205°.—This fraction possessed a pronounced odour of linalool:

0·1145 gave 0·3352 CO_2 and 0·1191 H_2O. C = 79·8; H = 11·6.
$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

Although this fraction still contained some terpene, it evidently consisted largely of an oxygenated substance. A portion of it was gently oxidised with a chromic acid mixture and the product extracted with ether. The ethereal liquid was washed, dried, and the ether removed, when a small amount of a product was obtained, which, on distillation, yielded a fraction possessing an intense lemon-like odour. The latter fraction, on treatment with β-naphthylamine and pyruvic acid, yielded the crystalline α-citryl-β-naphthacinchoninic acid, melting at 200°. This result, together with the positive rotation of the original fraction, rendered it evident that *d*-linalool was present in the oil.

No semicarbazone, oxime, or solid bisulphite compound could be obtained from the above fraction, thus indicating the absence of aldehydes or ketones.

The subsequent fractions of the oil, as previously noted, were all relatively small in amount, but they were analysed with the following results:

Fraction 205—215°.

0·1193 gave 0·3141 CO_2 and 0·1210 H_2O. C = 78·7; H = 11·3.

Fraction 215—225°.

0·1684 gave 0·4855 CO_2 and 0·1634 H_2O. C = 78·6; H = 10·8.

Fraction 225—235°.

0·1691 gave 0·4893 CO_2 and 0·1526 H_2O. C = 78·9; H = 10·0.

Fraction 235—245°.

0·1359 gave 0·3930 CO_2 and 0·1191 H_2O. C = 78·9; H = 9·7.

Fraction 245—255°.

0·2367 gave 0·6796 CO_2 and 0·2026 H_2O. C = 78·3; H = 9·5.

Fraction 255—265°.

0·1435 gave 0·4049 CO_2 and 0·1139 H_2O. C = 77·0; H = 8·8.

Fraction 265—275°.

0·1855 gave 0·5090 CO_2 and 0·1386 H_2O. C = 74·8; H = 8·3.

Fraction above 275°.—The amount of this fraction was only 5 grams and, being obviously of an indefinite character, it was not analysed.

The fractions collected between 195° and 245° were all fragrant liquids, whereas the odour of those obtained between 245° and 275° was not so distinctive.

As all the fractions which distilled above 195° under ordinary pressure were too small in amount to admit of a satisfactory examination, the nature of the oxygenated constituents of the oil was more fully determined by means of a larger quantity of material, designated as heavy oil of nutmeg, which was kindly supplied to us by Messrs. Stafford Allen & Sons. The identification of these constituents will therefore be described in connexion with the examination of the so-called "heavy oil of nutmeg" in the second section of this paper. It may here be noted, however, that among the above fractions those boiling at 255—265° and 265—275° respectively contained a considerable amount of myristicin, for they both readily yielded the dibromomyristicin dibromide, which crystallised in silky needles melting at 128—129° (*Ber.*, 1903, **36**, 3446).

Acids Obtained by the Hydrolysis of the Oil.

The alkaline, aqueous liquid obtained by the hydrolysis of the oil, as previously described, was acidified with sulphuric acid and distilled with steam. The distillate contained some oily drops, and towards the end of the operation a small amount of solid passed over. It was therefore extracted with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulphate, and the ether removed. About 1 gram of a dark brown, oily product was thus obtained, which was converted into a sodium salt, and from the latter five fractions of silver salts were prepared. These were washed, dried in a vacuum over sulphuric acid, and analysed :

Fraction	I.	0·1475 of	silver salt	gave	0·0459 Ag.	Ag = 31·1.
,,	II.	0·1107	,,	,,	,, 0·0366 Ag.	Ag = 33·1.
,,	III.	0·1213	,,	,,	,, 0·0534 Ag.	Ag = 44·0.
,,	IV.	0·1601	,,	,,	,, 0·0815 Ag.	Ag = 50·9.
,,	V.	0·1583	,,	,,	,, 0·0950 Ag.	Ag = 60·0.

It is evident from these results that the acids extracted by ether represented a rather complex mixture, apparently containing some myristic acid, since silver myristate requires Ag = 32·2 per cent. Their nature was, however, more fully ascertained by the subsequent examination of the corresponding product from "heavy oil of nutmeg."

The aqueous distillate, which had been extracted with ether as above-described, still contained some acid, which was converted into a barium salt. The hot solution of the latter, on cooling, deposited a quantity (about 2 grams) of a salt in glistening leaflets. This was collected, washed with a little water, dried at 110°, and analysed:

0·8933 of the dried salt gave 0·8135 $BaSO_4$. $Ba = 53·5$.

$(C_2H_3O_2)_2Ba$ requires $Ba = 53·7$ per cent.

By the evaporation of the mother liquors, a further quantity of a salt was obtained, the solution of which abundantly reduced mercuric chloride on heating. It was likewise dried at 110° and analysed:

1·4219 of the dried salt gave 1·4201 $BaSO_4$. $Ba = 58·7$.

$(CHO_2)_2Ba$ requires $Ba = 60·4$ per cent.

These results established the presence of esters of both formic and acetic acid in the oil.

The contents of the distillation flask, after the removal of the volatile acids by steam, were extracted with ether, but only a little resinous matter was obtained.

II.—*Examination of a Heavy Oil of Nutmeg.*

This oil, which, as previously stated, had been kindly supplied to us by Messrs. Stafford Allen & Sons, represented a product obtained by the rectification of very large quantities of normal oil of nutmeg, and consisted chiefly of the oxygenated constituents of the latter, the terpenes having been to a large extent removed. It was a pale yellow liquid, possessing the following constants: d 20°/20° = 1·102; a_D + 1°17′ in a 1-dcm. tube; saponification value 6·10.

Treatment with Sodium Hydroxide.—A quantity (6800 grams) of the oil was extracted several times with a 5 per cent. solution of sodium hydroxide. The combined alkaline liquids and washings were shaken with ether to remove any adhering oil, acidified with sulphuric acid, and the liberated acids and phenols extracted with ether. In order to remove the acids, the ethereal liquid was shaken with a 10 per cent. solution of sodium carbonate. The liquid obtained by extraction with the last-mentioned alkali, when acidified with sulphuric acid and distilled, yielded, however, only traces of acetic and butyric acids. No crystalline acid could subsequently be isolated from the contents of the distilling flask, and therefore the heavy oil, unlike the normal oil of nutmeg, did not contain any free myristic acid.

Identification of Eugenol and iso*Eugenol.*

The above-mentioned ethereal liquid, from which the traces of acid had been extracted, was washed with water, dried with anhydrous sodium sulphate, and the ether removed. About 100 grams of crude phenols were thus obtained, which were first distilled under diminished pressure to remove resinous matter, and then under the ordinary pressure, when the following fractions were collected: 245—250°; 250—260°; above 260°.

Fraction 245—250°.—This amounted to about 50 grams, and evidently consisted chiefly of eugenol. Its identity was confirmed by the formation of benzoyleugenol (m. p. 69°), and also of the diphenylurethane, melting at 107—108° (*Ber.*, 1907, **40**, 1834).

Fraction 250—260°.—This amounted to 25 grams. In attempting to prepare from it a diphenylurethane, it was found that the product did not solidify so readily as in the case of the preceding fraction, and was obviously a mixture. With consideration of the probable presence of *iso*eugenol, and as the *diphenylurethane* of the latter had not hitherto been prepared, a little of this derivative was made from pure *iso*eugenol (Kahlbaum) and found to melt at 112—113°, which is but a few degrees higher than the melting point of the corresponding derivative of eugenol. It was thus evident that the diphenylurethanes are not well adapted for the differentiation of the above-mentioned isomeric phenols.

Fraction above 260°.—This amounted to about 10 grams. It readily yielded a crystalline benzoyl derivative melting at 105°, thus confirming the observation recorded in connexion with the normal oil of nutmeg, that the phenols consist of a mixture of eugenol and *iso*eugenol.

Hydrolysis of the Oil.

After the removal of the phenols by extraction with a solution of sodium hydroxide, as above described, the oil was heated with an alcoholic solution of potassium hydroxide (1 part KOH to 100 parts of oil). The greater part of the alcohol was then removed, water added, and the separated oil collected, washed, and dried; the aqueous, alkaline liquid being reserved for the subsequent examination of the acids.

Fractional Distillation of the Hydrolysed Oil.

The hydrolysed oil was subjected to a systematic fractional distillation, the portions boiling below 265° being finally collected under the ordinary pressure, whilst the remainder of the oil was fractionated under a pressure of 40 mm. The following results were obtained:

Boiling-point.	d 20°/20.	α_D in a 1-dcm. tube.	Amount in grams.
Below 195	—	—	184
195—205	0·9136	+11 22′	35
205—215	0·9432	+11 31	440
215—225	0·9666	+ 5 5	238
225—235	1·0070	− 0 33	151
235—245	1·0469	− 0 5	82
245—255	1·0729	+ 1 4	74
255—265	1·1014	+ 1 48	182
165—169°/40 mm.	1·1316	+ 1 8	130
169—171 ,,	1·1341	+ 0 51	560
171—173 ,,	1·1437	+ 0 6	3420
Above 173 ,,	1·1366	± 0 0	60
		Total ...	5556 grams.

Fraction below 195°.—Since this fraction consisted chiefly of terpenes, which had been thoroughly investigated in connexion with the normal oil, it did not require further consideration.

Identification of Linalool.

Fraction 195—205°.—This was a colourless liquid, possessing the fragrant odour characteristic of linalool:

0·0988 gave 0·2881 CO_2 and 0·1046 H_2O. C = 79·5; H = 11·8.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

The analysis of this fraction indicated that it still contained a small amount of terpene. A quantity of it was gently oxidised with a chromic acid mixture, and the product extracted with ether, when, after the removal of the solvent, a small amount of a yellow liquid was obtained, which was distilled under the ordinary pressure. The portion boiling between 215° and 235° possessed an intense odour of citral, and readily yielded α-citryl-β-naphthacinchoninic acid, melting at 197°, thus confirming the presence of linalool in the oil.

Identification of Borneol and Terpineol, and Formation of a Diketone, $C_8H_{14}O_2$.

Fraction 205—215°.—This was a very large fraction. It was a colourless liquid, with an odour resembling that of terpineol:

0·1409 gave 0·4015 CO_2 and 0·1445 H_2O. C = 77·7; H = 11·4.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

Test for Terpineol.—A portion of the liquid was shaken with a concentrated solution of hydriodic acid (sp. gr. 1·96), when a heavy, dark-coloured oil was formed. This was separated from the aqueous layer, dissolved in ether, and shaken with a dilute solution of sodium bisulphite to remove the free iodine. The ethereal solution was washed, dried with anhydrous sodium sulphate, and the ether removed, when a thick oil was obtained which solidified in a freezing mixture. This solid was dried on a porous tile and crystallised from light petroleum, from which it separated in colourless prisms, melting at 80°. This melting point was identical with that of dipentene dihydriodide, $C_{10}H_{18}I_2$, prepared from terpineol (m. p. 35°), and, when the two preparations were intimately mixed, the melting point remained unchanged. It was thus evident that this fraction of the oil contained a considerable amount of terpineol, and its presence was confirmed by the isolation of the ketolactone, $C_{10}H_{16}O_3$, from the products of its oxidation.

Oxidation of the Fraction. Formation of the Ketolactone, $C_{10}H_{16}O_3$, *a Diketone*, $C_8H_{14}O_2$, *and Camphor*.—A quantity (150 grams) of the fraction (b. p. 205—215°) was oxidised with a chromic acid mixture in the proportions of potassium dichromate (8 parts), sulphuric acid (12 parts), and water (36 parts) to 1 part of oil. In the beginning of the oxidation the odour developed was that of citral, but finally it became distinctly camphoraceous. After the mixture had been gently heated on a water-bath for about an hour, it was allowed to cool, and then extracted several times with ether. The ethereal liquid was first washed with a solution of sodium carbonate to free it from acidic substances, then with water, and the ether removed. A yellow oil was thus obtained, which was distilled with steam, when the greater portion passed over. The non-volatile portion of the oxidation product was extracted by ether, the ethereal solution being washed, dried, and the ether removed. A small quantity of a viscid, brown oil was thus obtained, which deposited no solid, even on long standing. It was finally distilled under diminished pressure, when the fraction of highest boiling point was obtained as a viscid, yellow liquid, which solidified when stirred with light petroleum. This solid was dried on a porous tile and crystallised from ether, from which it separated in colourless prisms melting at 62—63°:

0·1165 gave 0·2782 CO_2 and 0·0907 H_2O. C = 65·1; H = 8·7.

$C_{10}H_{16}O_3$ requires C = 65·2; H = 8·7 per cent.

It is evident that this substance is identical with the ketolactone, $C_{10}H_{16}O_3$ (m. p. 64°), which was obtained by Wallach by the oxidation of terpineol with chromic acid. As it is the optically inactive modification of the ketolactone, it follows that the terpineol contained in the oil must be the racemic form (compare Wagner and Brickner, *Ber.*, 1899, **32**, 2315).

The portion of the above-mentioned oxidation product which was volatile in steam possessed a strongly camphoraceous odour, although no solid substance separated. The distillate was then extracted with ether, the ethereal solution dried, and the solvent removed, when a quantity of an oily liquid was obtained. One part of this oil, in alcoholic solution, was heated for some time on a water-bath with hydroxylamine hydrochloride (1 part) and sodium hydroxide (1·5 parts), after which water was added and the mixture carefully neutralised with sulphuric acid. As no solid oxime separated, the mixture was extracted with ether, the ethereal solution being washed, dried, and the solvent removed, when a brown oil was obtained which solidified on stirring with light petroleum. This solid substance was collected on a filter and crystallised from hot alcohol, from which, on cooling, it separated in small, rectangular prisms melting at 140°. The yield of this compound was about 3 grams:

0·1368 gave 0·2804 CO_2 and 0·1187 H_2O. C = 55·9; H = 9·6.
0·1534 ,, 0·3137 CO_2 ,, 0·1272 H_2O. C = 55·8; H = 9·2.
0·1998 ,, 27·4 c.c. moist nitrogen at 16·5° and 762 mm. N = 16·1.
$C_8H_{16}O_2N_2$ requires C = 55·8; H = 9·3; N = 16·3 per cent.

From these results, it appears highly probable that this compound is the *dioxime* of a *diketone*, $C_8H_{14}O_2$. The only known compound of the formula $C_8H_{16}O_2N_2$ with which it might be identical is the dioxime of ethyl butyl diketone,

$CH_3{\cdot}CH_2{\cdot}C(:NOH){\cdot}C(:NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$

(m. p. 139—141°), which has been described by Fileti and Ponzio (*J. pr. Chem.*, 1898, [ii], **58**, 364). These authors also prepared an osazone, which was found to melt at 96—97°. With the object of ascertaining whether our dioxime is identical with that prepared by Fileti and Ponzio, 50 grams of the fraction (b. p. 205—215°) were oxidised as previously described, and the portion of the oxidation product which was volatile in steam treated with an excess of phenylhydrazine in alcoholic solution. No solid osazone could, however, be obtained from the product of the reaction. An attempt was also made to obtain a semicarbazone of the diketone, $C_8H_{14}O_2$, from the volatile oxidation product of the fraction 205—215°, but without success. These results therefore do not permit of any conclusion respecting the identity of the compound $C_8H_{16}O_2N_2$, here described, with the dioxime of ethyl butyl diketone prepared by Fileti and Ponzio (*loc. cit.*).

The *dioxime*, $C_8H_{16}O_2N_2$, is a colourless, odourless substance, sparingly soluble in cold, but readily in hot, alcohol. It is also soluble in warm ethyl acetate, from which it crystallises in fine needles, but is only sparingly soluble in benzene, and insoluble in light petroleum and in water. When warmed with dilute sulphuric acid, it first dissolved, developing a fragrant odour, but, as resinification ensued, it was impossible by this means to regenerate the ketone from which it had been formed.

Since not more than a trace of substance of aldehydic or ketonic nature was present in the fraction of the oil employed, it is evident that the above-mentioned diketone must represent the oxidation product of an unidentified compound, which is doubtless an *alcohol*.

The light petroleum liquid which had been separated from the dioxime, as above described, possessed a strongly camphoraceous odour. After the removal of the solvent, a brown oil was obtained which did not solidify, and was therefore distilled under diminished pressure. From the first portions of the distillate a solid separated which had the characteristic odour of camphor, and, after drying on a porous tile, melted at 170—175°. This substance readily yielded a semicarbazone melting at 238°, and when the latter was mixed with camphorsemicarbazone the melting point remained unchanged. Not having obtained the camphor in the form of its oxime by the treatment of the original product of oxidation with hydroxylamine, it may be assumed that the amount of the latter was only sufficient to combine with the diketone which was present in the mixture.

The identification of camphor as a product of oxidation of the fraction boiling between 205° and 215° affords conclusive evidence of the presence of borneol in the original oil.

Identification of Geraniol.

Fraction 215—225°.—This was a comparatively large fraction. It was a colourless liquid, possessing a rose-like odour:

0·1109 gave 0·3136 CO_2 and 0·1055 H_2O. C = 77·1; H = 10·6.

This fraction was found to contain some terpineol, since it readily yielded the crystalline dipentene dihydriodide (m. p. 80°) on treatment with concentrated hydriodic acid, whilst the analytical results also indicated it to contain some of the constituents of the succeeding fraction.

A portion of the fraction was oxidised with a chromic acid mixture, when the odour of citral was at first strongly developed, and from the final product a further small amount of the diketone, $C_8H_{14}O_2$, was obtained in the form of its dioxime (m. p. 140°), which has been described in connexion with the preceding fraction.

As the odour of the fraction, together with the evident formation of citral by its limited oxidation, indicated the presence of geraniol, a portion of it was treated with diphenylcarbamic chloride in the presence of pyridine, according to the method suggested by Erdmann (*J. pr. Chem.*, 1897, [ii], 56, 8), when a product was obtained which crystallised from alcohol in thin, colourless needles melting at 81—82°. This was found to be identical with the diphenylurethane (m. p. 82°)

prepared from a specimen of pure geraniol, and the presence of the latter compound in the oil was therefore established.

Identification of Safrole.

Fraction 225—235°.—This was a pale yellow liquid, possessing a distinct odour of safrole, and also the rose-like odour of geraniol :

0·1129 gave 0·3154 CO_2 and 0·0933 H_2O. $C = 76·2$; $H = 9·2$.

The presence of a considerable proportion of geraniol in this fraction was evident from the fact that it yielded the diphenylurethane (m. p. 82°), and, when gently oxidised, some citral was obtained, which was identified by the formation of the α-citryl-β-naphthacinchoninic acid, melting at 195—197°. The odour of the fraction, together with its high density and the analytical figures, indicated, however, that it also contained safrole.

A portion was oxidised with a mixture consisting of potassium dichromate (8 parts), sulphuric acid (12 parts), and water (30 parts) to 1 part of oil. After heating gently for two hours, a distinct odour of piperonal was observed. The mixture, after being allowed to cool, was repeatedly extracted with ether, the ethereal liquids washed first with water, then with aqueous sodium carbonate, which removed only a trace of acidic substance, finally again with water, and the ether removed. A brown, oily residue was thus obtained, which was shaken with a saturated solution of sodium bisulphite, when a small amount of a solid compound separated. This was collected on a filter by the aid of the pump, and washed with ether. On warming with dilute alkali, a substance was liberated which had the odour of piperonal. This alkaline liquid was subsequently extracted with ether, the ethereal solution being washed, dried, and the ether removed. The residual oily liquid was placed in a freezing mixture and nucleated with a trace of piperonal, when crystallisation ensued, and the resulting product melted at 34—35°. This was identified as piperonal, thus proving the presence of safrole in the oil.

The fraction (b. p. 225—235°), as well as the two preceding ones, were treated with semicarbazide hydrochloride and sodium acetate in alcoholic solution, and the uncombined oil subsequently removed by distillation with steam, when a very small amount of a solid semicarbazone was obtained. On treatment with dilute sulphuric acid, this yielded a few drops of a yellow oil, which possessed an odour resembling that of citral, but gave a *β-naphthacinchoninic acid* derivative which, when crystallised from alcohol, separated in pearly leaflets melting at 248° with decomposition. The substance, evidently an *aldehyde*, which yielded this derivative was so small in amount that it was impossible further to characterise it.

As this fraction of the oil was slightly lævorotatory, it must have contained a small amount of some undetermined substance, for both geraniol and safrole are optically inactive, and the preceding, as well as the principal succeeding, fractions were dextrorotatory.

Fraction 235—245°.—This was a colourless liquid, possessing a strong odour of safrole:

0·2001 gave 0·5502 CO_2 and 0·1417 H_2O. C = 75·0; H = 7·9.

The presence of safrole was proved, as described in connexion with the preceding fraction, by the isolation of a small quantity of piperonal, melting at 33—35°, from the products of its oxidation.

Fraction 245—255°.—This was a colourless liquid, which became slightly yellow on standing. It was comparatively small in amount:

0·1502 gave 0·4126 CO_2 and 0·1021 H_2O. C = 74·9; H = 7·6.

This fraction was specially tested for the methyl ether of eugenol, but with a negative result, since it yielded neither the corresponding bromo-derivative nor could any veratric acid be isolated from the products of its oxidation. On oxidation, however, it developed a strong odour of piperonal, indicating the presence of safrole, and yielded on treatment with bromine a compound which crystallised from alcohol in small needles melting sharply at 128—129°. This was identified as the bromo-derivative of myristicin, which will subsequently be described.

Fraction 255—265°.—This was considerable in amount:

0·1550 gave 0·4048 CO_2 and 0·0984 H_2O. C = 71·2; H = 7·1.

It was evident that this fraction consisted largely of myristicin, together with a small amount of some dextrorotatory substance, probably a sesquiterpene, which it was impossible to isolate.

The subsequent fractions, which had been distilled under diminished pressure, were analysed with the following results:

Fraction 165—169°/40 mm.

0·1500 gave 0·3854 CO_2 and 0·0956 H_2O. C = 70·1; H = 7·1.

Fraction 169—171°/40 mm.

0·1737 gave 0·4457 CO_2 and 0·1089 H_2O. C = 70·0; H = 7·0.

Each of these fractions evidently consisted chiefly of the constituent of the following fraction.

Identification of Myristicin, $C_{11}H_{12}O_3$.

Fraction 171—173°/40 mm.—This was by far the largest fraction of the heavy oil of nutmeg, amounting to 3420 grams, or more than one-half of the total quantity of oil employed. When freshly distilled, it was a colourless liquid, possessing only a faintly aromatic odour:

0·1469 gave 0·3728 CO_2 and 0·0844 H_2O. C = 69·2 ; H = 6·4.
0·1135 „ 0·2875 CO_2 „ 0·0677 H_2O. C = 69·1 ; H = 6·6.
0·2424 „ 0·6098 CO_2 „ 0·1400 H_2O. C = 68·6 ; H = 6·4.
$C_{11}H_{12}O_3$ requires C = 68·7 ; H = 6·2 per cent.

d 20°/20° = 1·1437 ; α_D + 0°6′ in a 1-dem. tube ; $n_D^{20°}$ 1·54032.

The results of analysis and the determination of the physical constants of this fraction rendered it evident that it consisted of nearly pure myristicin. This compound has previously been obtained from material designated as mace oil (Thoms, *Ber.*, 1903, **36**, 3446), but proof of its occurrence in oil of nutmeg has hitherto been lacking.

Dibromomyristicin Dibromide, $C_{11}H_{10}O_3Br_4$.—This was prepared according to the method described by Thoms (*loc. cit.*). When crystallised from a mixture of alcohol and ethyl acetate, it separated in fine, colourless, silky needles, melting at 128—129°:

0·2085 gave 0·2000 CO_2 and 0·0402 H_2O. C = 26·2 ; H = 2·1.
$C_{11}H_{10}O_3Br_4$ requires C = 25·9 ; H = 2·0 per cent.

Thoms described this compound as a white, crystalline powder, melting at 130°.

iso*Myristicin*.—A quantity (20 grams) of the fraction (b. p. 171—173°/40 mm.) was heated on a water-bath for two days with an alcoholic solution of 50 grams of potassium hydroxide, and the product extracted with ether. After the removal of the solvent, it was distilled under diminished pressure, when practically all passed over at 166°/18 mm. as a colourless, viscid liquid, which, when placed in a freezing mixture, readily solidified. It was crystallised from alcohol, from which it separated in radiating clusters of needles, melting at 44°:

0·1345 gave 0·3380 CO_2 and 0·0757 H_2O. C = 68·5 ; H = 6·3.
$C_{11}H_{12}O_3$ requires C = 68·7 ; H = 6·2 per cent.

The refractive index of this substance, kindly determined for us by Mr. Frederic H. Lees, was $n_D^{45.5}$ 1·56551, whereas that of myristicin at the same temperature was 1·52927.

*Dibromo*iso*myristicin Dibromide*.—This was easily prepared by the same method as that employed for the corresponding bromo-derivative of myristicin. When crystallised from a mixture of alcohol and ethyl acetate, it separated in stout needles, melting at 156°:

0·2013 gave 0·1915 CO_2 and 0·0406 H_2O. C = 25·9 ; H = 2·2.
$C_{11}H_{10}O_3Br_4$ requires C = 25·9 ; H = 2·0 per cent.

Acids Obtained by the Hydrolysis of the Heavy Oil of Nutmeg.

The alkaline liquid and aqueous washings obtained by the hydrolysis of the oil, as previously described, were concentrated, acidified with sulphuric acid, and distilled with steam. The distillate contained a quantity of acids in the form of a pale yellow oil, which was extracted by means of ether. From the aqueous liquid, which was still strongly acid, about 20 grams of a barium salt were obtained. This was fractionally crystallised, and each fraction analysed, when it was found to consist entirely of barium acetate.

Fraction I. 0·8950 of the salt gave 0·8106 $BaSO_4$. Ba = 53·3.
,, II. 0·7924 ,, ,, 0·7247 $BaSO_4$. Ba = 53·8.
,, III. 0·4997 ,, ,, 0·4573 $BaSO_4$. Ba = 53·8.
,, IV. 0·7443 ,, ,, 0·6802 $BaSO_4$. Ba = 53·7.
$(C_2H_3O_2)_2Ba$ requires Ba = 53·7 per cent.

The pale yellow, oily acids which had been extracted from the distillate by means of ether, as above described, amounted to about 6 grams. These were distilled under the ordinary pressure up to 270°, and the remainder at 20 mm. pressure, when the following fractions were obtained: (*a*) below 230°; (*b*) 230—250°; (*c*) 250—270°/760 mm.; (*d*) 190—230°/20 mm. Each of these fractions was converted into a sodium salt, from which, by fractional precipitation with a solution of silver nitrate, a number of silver salts were prepared. These were washed, dried in a vacuum over sulphuric acid, and analysed:

(*a*) 0·0882 gave 0·0386 Ag. Ag = 43·8.
(*b*) 0·1150 gave 0·0492 Ag. Ag = 42·8.
0·1835 ,, 0·0789 Ag. Ag = 43·0.
0·1531 ,, 0·0664 Ag. Ag = 43·4.
0·1752 ,, 0·0790 Ag. Ag = 45·1.
(*c*) 0·1044 gave 0·0434 Ag. Ag = 41·6.
0·1862 ,, 0·0806 Ag. Ag = 43·3.
0·1751 ,, 0·0765 Ag. Ag = 43·7.
0·1231 ,, 0·0544 Ag. Ag = 44·2.
(*d*) 0·1272 gave 0·0503 Ag. Ag = 39·5.
0·2145 ,, 0·0856 Ag. Ag = 39·9.
0·2309 ,, 0·0968 Ag. Ag = 41·9.
$C_8H_{15}O_2Ag$ requires Ag = 43·0 per cent.
$C_9H_{17}O_2Ag$,, Ag = 40·8 ,, ,,

It would appear from these results that the volatile, oily acids obtained by the hydrolysis of nutmeg oil contain a considerable proportion of an octoic acid, with smaller amounts of acids of higher and lower molecular weight.

Isolation of a New Monocarboxylic Acid, $C_{12}H_{17}O{\cdot}CO_2H$.

After the removal of the volatile acids by distillation with steam, as above described, there remained in the distillation flask a semi-solid mass. This was spread on a porous plate, when a quantity of tarry matter became absorbed and a crystalline solid was obtained. The latter was purified by dissolving it in hot dilute acetic acid, from which it crystallised in hexagonal prisms, melting at 84—85°, which possessed a slightly yellow tint. When crystallised from dilute alcohol, it separated in needles. The substance is extremely soluble in the usual organic solvents, but is insoluble in water:

0·1150 gave 0·2972 CO_2 and 0·0861 H_2O. C = 70·4; H = 8·3.
0·1015 ,, 0·2620 CO_2 ,, 0·0758 H_2O. C = 70·4; H = 8·3.
$C_{13}H_{18}O_3$ requires C = 70·3; H = 8·1 per cent.

0·1640, in alcoholic solution, neutralised 7·4 c.c. N/10 NaOH.
$C_{12}H_{17}O{\cdot}CO_2H$ requires 7·4 c.c.

The only known monocarboxylic acid of the formula $C_{13}H_{18}O_3$ possessing properties similar to those of the above compound is carvacroxypropionic acid, which has been described by Bischoff (*Ber.*, 1900, **33**, 1270) as forming colourless prisms, melting at 81·5—82·5°. A specimen of the latter acid was therefore prepared for the purpose of comparison with the above described compound, but the two substances were found to be not identical. The substance isolated from nutmeg oil is therefore to be regarded as a new *monocarboxylic acid*, $C_{12}H_{17}O{\cdot}CO_2H$.

Summary.

The results of this investigation have shown that the essential oil of nutmeg contains the following substances:

1. Eugenol, } about 0·2 per cent.
2. *iso*Eugenol, }
3. *d*-Pinene, } about 80 per cent.
4. *d*-Camphene, }
5. Dipentene, about 8 per cent.
6. *d*-Linalool, }
7. *d*-Borneol, } about 6 per cent.
8. *i*-Terpineol, }
9. Geraniol, }

10. A new *alcohol*, yielding on oxidation a *diketone*, $C_8H_{14}O_2$, in very small amount.

11. A trace of an *aldehyde* resembling citral, but yielding a *β-naphthacinchoninic acid* derivative melting at 248°.

12. Safrole, about 0·6 per cent.

13. Myristicin, $C_{11}H_{12}O_3$, about 4 per cent.

14. Myristic acid, in the free state, about 0·3 per cent., and apparently a small amount in the form of esters.

15. Formic, acetic, butyric, and octoic acids, and a new *mono-*

carboxylic acid, $C_{13}H_{18}O_3$, all in the form of esters, and in relatively small amount.

Although the proportions of the above-mentioned constituents are those indicated for what we have designated a normal oil of nutmeg, it is obvious that as the latter differed in its physical characters, particularly in its optical rotatory power, from the standards generally adopted for this oil, the composition is subject to considerable variation, according to the character of the material employed for distillation.

This investigation has, furthermore, shown that the portion of nutmeg oil which has hitherto been designated "myristicol" is a mixture of alcohols, of which terpineol appears to be the predominating constituent.

In view of the fact that narcotic properties are attributed to the nutmeg, the authors are at present engaged in an investigation of its constituents other than the essential oil.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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CCI.—*The Resolution of* sec.-*Octyl Alcohol* [*Methylhexylcarbinol. Octane-2-ol*].

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

THE method described by one of us and W. O. Littlebury (Trans., 1906, 89, 467) for the resolution of racemic alcohols by the fractional crystallisation of an ester of *l*-menthylcarbamic acid fails in the case of *sec.*-octyl alcohol, as the ester formed by this alcohol is an oil. The resolution, however, is readily effected by another method recently described by one of us and W. O. Littlebury (this vol., 1973) and used for the preparation of pure *d*- and *l-iso*borneol.

Phthalic anhydride combines readily with *sec.*-octyl alcohol, and the resulting acid ester is almost quantitatively resolved by the crystallisation, first of the brucine salt and then of the cinchonidine salt, of the acid ester obtained from the more soluble portion of the brucine salt.

The active alcohol is very stable and not readily racemised, whilst the ease with which both optical isomerides can be obtained renders this alcohol more convenient than any other for experiments in which both the dextro- and lævo-forms are required.

It has already been shown by Marckwald and McKenzie (*Ber.*, 1904, 34, 469) that commercial *sec.*-octyl alcohol, which is made by heating castor oil with potash, is a mixture of the inactive compound with some of the lævo-alcohol, and that the same can be partially resolved by fractional esterification with *d*-tartaric acid. However, the maximum rotation of the product obtained by their method was not greater than $[\alpha]_D$ 1°, whereas the pure alcohol has $[\alpha]_D$ 9·8°.

We hope shortly to communicate to the Society results of similar experiments carried out with the simpler aliphatic alcohols.

EXPERIMENTAL.

The octyl alcohol used in our experiments was Kahlbaum's II quality. In a 2-dcm. tube, it gave α −0·15°.

(d + l)sec.-*Octyl Hydrogen Phthalate*, $C_8H_{17}O_2 \cdot C_6H_7 \cdot CO_2H$.—Equal molecules of *sec.*-octyl alcohol and phthalic anhydride are heated at 110—120° for fifteen hours. An excess of ethyl alcohol is added, and the mixture heated on the water-bath. The mass is dissolved in sodium carbonate solution, which is extracted with light petroleum to remove traces of neutral esters, unchanged alcohol, and ketonic impurities of the commercial alcohol. The alkaline solution is acidified, and the acid ester extracted with ether and crystallised twice from light petroleum. The crystalline mass obtained melts at 55°, and is very soluble in benzene, alcohol, chloroform, and either warm acetone or acetic acid, from which it may also be readily recrystallised.

l-*Brucine* d-sec.-*Octyl Hydrogen Phthalate.*—Sixty-five grams of the inactive acid ester are dissolved in about 1 litre of acetone and boiled under a reflux condenser with 92 grams of brucine. After the alkaloid has dissolved, the solution, when cold, deposits clusters of hard, prismatic crystals of the salt, which melt at 146—148° and have $[\alpha]_D$ −6·7° in ethyl-alcoholic solution. Two recrystallisations from acetone give the pure salt, which melts at 151°. The mother liquors can be worked up and give a further crop of the pure salt, the total yield being about 73 grams. Analysis shows the salt to be composed of 1 molecule of each component (N found 4·4, instead of 4·2 per cent.). The specific rotation of the salt is $[\alpha]_D$ −5·44° in ethyl-alcoholic solution ($c = 5$), and this as well as the melting point is unaltered by six recrystallisations from acetone.

d-sec.-*Octyl Hydrogen Phthalate.*—The brucine salt is dissolved in a small quantity of alcohol and poured into dilute hydrochloric acid. The precipitated acid ester crystallises very readily from a large quantity of light petroleum in large, stout prisms, which melt at 75°. When titrated, 0·4492 neutralised 0·0644 gram NaOH; theory requires 0·0646 gram. The following polarimetric observations were made in a 2-dcm. tube:

0·9617, made up to 20 c.c. with chloroform, gave α +4·13°, whence $[\alpha]_D$ +42·94°.

1·0150, made up to 20 c.c. with ethyl alcohol, gave α +4·88°, whence $[\alpha]_D$ +48·08°.

These specific rotations were unaltered by recrystallisation of the substance.

l-*Cinchonidine* l-sec.-*Octyl Phthalate.*—The mother liquors from the brucine salt are precipitated by hydrochloric acid, and yield an acid ester which has $[\alpha]_D$ −42·4° in ethyl-alcoholic solution. The cinchonidine salt is prepared in a similar manner to the brucine salt. It crystallises from aqueous acetone in long, felted needles, and after six recrystallisations melts indefinitely between 112° and 116°, and has a constant rotation:

0·9497, made up to 20 c.c. with ethyl alcohol, gave α −6·46° in a 2-dcm. tube, whence $[\alpha]_D$ −68·02°.

l-sec.-*Octyl hydrogen phthalate* is easily obtained from the cinchonidine salt. It crystallises from light petroleum in lustrous prisms very similar in appearance to those of the dextro-ester, and melts at 75°. When titrated, 0·4543 neutralised 0·0652 gram NaOH; theory requires 0·0653 gram. The specific rotation is practically identical with that of the optical antipode:

0·9635, made up to 20 c.c. with chloroform, gave α −4·17° in a 2-dcm. tube, whence $[\alpha]_D$ −43·27°.

1·0049, made up to 20 c.c. with ethyl alcohol, gave α −4·85° in a 2-dcm. tube, whence $[\alpha]_D$ −48·26°.

A mixture of approximately equal quantities of the two phthalates melted indefinitely at abou 5

d-sec.-*Octyl Alcohol.*—The active acid esters readily dissolve in aqueous potash, and are quickly hydrolysed, when the solution is boiled. The alcohol, being insoluble in alkaline solutions, is easily extracted by ether, and is then fractionated under reduced pressure. Several comparative experiments were carried out with the dextro-ester, and these alone are recorded. The following are the rotations observed with three separate preparations: in I the acid ester was hydrolysed with the calculated amount of potash; in II it was partially hydrolysed wi twice the calculated amount; in III the residue from II was hydr lysed completely with a large excess of potash:

I.	In a	50 mm.	tube at 17°	gave α +	4·00°.
II.	,,	100 mm.	,, 17°	,,	8·00°.
III.	,,	24·96 mm.	,, 20°	,,	1·99°.
I + II.	,,	200 mm.	,, 20°	,,	15·93°.

Similar products to these were mixed and redistilled twice, when the pure *d-sec.*-octyl alcohol boiled at 86°/20 mm. The density found was D_4^{20} 0·8221 and D_4^{17} 0·8229, this being slightly higher than recorded by Brühl (*Annalen*, 1880, **203**, 28), who gave D_4^{20} 0·8193 for the racemic alcohol.

The refractive index was found to be n_D^{20} 1·424, whence the molecular refraction is 40·28, the calculated value being 40·44.

The rotation was observed in a 2-dcm. tube at 17°, the mean of thirteen concordant readings being $\alpha + 8{\cdot}125°$, whence $[\alpha]_D^{17} + 9{\cdot}87°$. It was also observed in solution:

1·0335, made up to 20 c.c. with chloroform, gave $\alpha + 0{\cdot}93°$ in a 2-dcm. tube, whence $\alpha_D + 9{\cdot}00°$.

1·0923, made up to 20 c.c. with ethyl alcohol, gave $\alpha + 1{\cdot}07$ in a 2-dcm. tube, whence $[\alpha]_D + 9{\cdot}79°$.

The pure dextro-alcohol was reconverted into the acid phthalate, which without recrystallisation had $[\alpha]_D + 48{\cdot}19°$ in ethyl alcohol.

Our thanks are due to Mr. Tom Thornley, who carried out preliminary work in the preparation of this and several other racemic acid phthalic esters, as also to the Research Fund Committee of the Society for a grant which has defrayed much of the cost of this investigation.

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CCII.—*The Alkyl Compounds of Gold.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

THE discovery that organo-metallic compounds can in many cases be conveniently prepared by the action of zinc ethyl on the halogen compounds of the metals was made by Buckton (*Proc. Roy. Soc.*, 1859, **9**, 309); he thus obtained mercury diethyl, lead tetraethyl, and tin tetraethyl, but was unable to apply the same reaction to the preparation of alkyl compounds of silver, platinum, or copper. Pope and Peachey showed (Proc., 1903, **19**, 290) that the alkyl tin compounds are conveniently prepared by the action of the Grignard reagent on stannic chloride or on halogen derivatives of the organo-tin compounds; since that time, a series of papers on the same reaction and its developments has appeared by Pfeiffer and his collaborators (*Ber.*, 1904, **39**, 319, 1125, 4617, &c.), but these authors have apparently overlooked the English work on the subject. From this and allied work, it has been learnt that alkyl compounds, such as those of tin, silicon, mercury, &c., can be readily prepared by the action of alkyl magnesium halogen derivatives on the halogen compounds of the elements. By the use of the Grignard reagent, there have hitherto been prepared representatives of classes of alkyl compounds of those elements which belong to groups II to VII of the periodic classification; the existence of these was either demonstrated or foreseen by Frankland (*Journ. Chem. Soc.*, 1850, **2**, 297).

Pope and Peachey have, however, recently prepared trimethylplatinic hydroxide and its salts by the aid of the Grignard reagent (Proc., 1907, **23**, 86), and in the present paper we describe the preparation of diethylauric bromide by the aid of magnesium ethyl bromide. We are thus now acquainted with organo-metallic compounds of elements of groups I to VIII of the periodic classification, and can consequently conclude that members of all the eight vertical groups yield stable alkyl compounds. In his original periodic table, Mendeléeff places gold and platinum in the horizontal series 10 (*Annalen*, 1871, *Supp.-Bd.*, **8**, 151); this is of interest in connexion with his conclusion that elements occurring in the higher even-numbered series do not yield stable alkyl compounds, and that if alkyl compounds were obtainable from such elements they would be totally different in properties from previously known organo-metallic substances. Trimethylplatinic iodide and diethylauric bromide are salt-like substances of constitutions according with the quadrivalency of platinum and the tervalency of gold; they correspond roughly in properties with such substances as triethylstannic and diethylthallic salts, so that it does not appear legitimate to conclude that Mendeléeff's prediction is verified by the discovery of the alkyl compounds of platinum and gold.

Evidence was obtained by Wanklyn and by Frankland (*Proc. Roy. Soc.*, 1859, **9**, 341, 345) of the existence of potassium and sodium ethyl, C_2H_5K and C_2H_5Na; although neither substance was isolated, it appears from the experimental facts quoted by these authors that ethyl iodide acts on sodium ethyl with formation of sodium iodide and gaseous products. No indication was obtained of the production of a compound having the composition $(C_2H_5)_2NaI$. In the case of the organo-gold compounds, behaviour the converse of this has been observed; there seems to be no tendency towards the production of the simpler substance, C_2H_5Au, but the more complex compound, $(C_2H_5)_2AuBr$, has been prepared. These facts perhaps illustrate better than has been hitherto possible one well-recognised aspect of the periodic law. In a high group of the periodic table, group V, for example, whilst triethylphosphine readily combines with ethyl iodide, triethylbismuthine does not; the tendency of the tervalent element to become quinquevalent diminishes as the atomic weight increases. In the low numbered group I, the converse is to be concluded from the facts that the substances, C_2H_5Na and $(C_2H_5)_2AuBr$, are known, whilst the compounds, C_2H_5Au and $(C_2H_5)_2NaI$, have not yet been prepared.

Diethylauric Bromide, $(C_2H_5)_2AuBr$.

As the preparation of diethylauric bromide presents some experimental difficulties, it will be convenient to state precisely the conditions under which we have been able to obtain the substance. Magnesium (5 grams) is converted into magnesium ethyl bromide by treatment with the calculated quantity of ethyl bromide dissolved in anhydrous ether (200 c.c.), care being taken that no excess of magnesium is left in the solution. The solution of the Grignard reagent is then run very slowly into a solution of dry auric bromide (22 grams) in ether (150 c.c.) by means of a dropping funnel; the latter solution is well cooled by a mixture of ice and salt, and constantly stirred during the process. Reaction is instantaneous, and during the admixture metallic gold begins to separate out; as soon as the whole of the Grignard reagent has been run in, powdered ice is cautiously added and the mixture then allowed to warm up to the room temperature; water and dilute acetic acid are then added, and the liquid extracted several times with light petroleum. The petroleum extract is washed several times with water and transferred to a large basin, which is then placed in a warm draught cupboard so that the petroleum is caused to evaporate rapidly at a temperature of 25—30°. When evaporation is complete, an almost colourless, crystalline residue is left in the basin and this, after one crystallisation by spontaneous evaporation of its solution in light petroleum, yields pure diethylauric bromide. Under the most favourable circumstances, a yield of 2 to 3 grams of the pure substance is obtained from the quantities named above.

The auric bromide used in this method of preparation can be replaced by auric chloride without diminishing the yield, but no larger yield was obtained on mixing the auric bromide and magnesium ethyl bromide solutions at the temperature of boiling liquid air. The yield is diminished by running the auric bromide solution into that of the Grignard reagent. Attempts to prepare the substance by the action of zinc ethyl on auric chloride, both in ethereal solution, were unsuccessful; the two solutions react with great violence, metallic gold is deposited, and no organic product can be isolated.

Diethylauric bromide crystallises from light petroleum in long, colourless, doubly-refracting needles, which melt at 58° with slight decomposition and have an odour resembling that of monobromocamphor. It is very soluble in benzene, petroleum, chloroform, or ether, much less so in alcohol, and insoluble in water. The substance volatilises readily at the ordinary temperature in air or in a vacuum, and would doubtless lend itself to vapour density determinations; when heated to about 70°, it decomposes explosively, leaving a residue of the metal and giving volatile products which, from their odour, do not consist of simple hydrocarbons, like butane, or of halogen derivatives of the same.

The analysis of the compound is conveniently effected by dissolving the substance in chloroform, adding a chloroform solution of bromine, slowly evaporating to dryness, and weighing the residue of gold obtained after ignition:

0·2082 gave 0·1216 Au. Au = 58·41.

$(C_2H_5)_2AuBr$ requires Au = 58·82 per cent.

Diethylauric bromide is extremely sensitive to reagents. It gives a precipitate of silver bromide with solutions of silver salts, and is at once acted on by bromine, ammonia, or nitric acid. When exposed to light in contact with water, metallic gold is gradually formed; reduction also takes place rapidly when its solutions are warmed, so that the crystallisation of diethylauric bromide from all but the most volatile solvents is difficult.

Monoethylauric Dibromide, $(C_2H_5)AuBr_2$.

On adding a dilute solution of bromine in chloroform to a solution of an equimolecular proportion of diethylauric bromide in the same solvent and allowing the solution to remain at the ordinary temperature, crystals of monoethylauric dibromide are gradually deposited. After most of the chloroform has spontaneously evaporated, the crystalline deposit is separated and washed with chloroform.

Monoethylauric dibromide is sparingly soluble in the ordinary organic solvents, and is moderately soluble in warm water. It crystallises in transparent, dark ruby-red, doubly-refracting prisms with square ends; on heating, it decomposes gradually without melting. It was analysed by decomposing a known weight with a chloroform solution of bromine and weighing the metal remaining after ignition:

0·3292 gave 0·1682 Au. Au = 51·09.
$(C_2H_5)AuBr_2$ requires Au = 51·07 per cent.

This compound is much more stable than diethylauric bromide, as is seen from the fact that its solutions may be heated to a much higher temperature than those of the latter without the occurrence of reduction. It is immediately converted by ammonia into a bright yellow powder, which is insoluble in water or acetone; this product detonates violently on gentle heating.

It is interesting to note that, whilst diethylauric bromide is quite colourless, monoethylauric dibromide possesses a red colour almost, although not quite, as deep as that of auric bromide.

Amminodiethylauric Bromide, $(C_2H_5)_2AuBr,NH_3$.

On gently warming diethylauric bromide with dilute aqueous ammonia, solution rapidly occurs, and after evaporation in a vacuum over sulphuric acid a white, crystalline substance remains. The product may be recrystallised from benzene, and forms transparent, doubly-refracting, colourless needles, which decompose gradually on heating at about 60°. It is soluble in benzene, acetone, chloroform, dilute ammonia, or dilute hydrochloric acid; the solution in hydrochloric acid may be boiled without the occurrence of reduction, and the solution is not precipitated by platinic chloride, although on prolonged standing metallic gold is deposited. The aqueous acetone solution gives a precipitate of silver bromide with silver salts.

For analysis, a weighed quantity of the substance was treated with a chloroform solution of bromine, as in the previous cases, and the residue ignited and weighed as metal. The reaction with the bromine solution is much more violent than in the other cases:

0·1308 gave 0·0728 Au. Au = 55·66.
$(C_2H_5)_2AuBr,NH_3$ requires Au = 55·98 per cent.

This substance appears to be the first ammino-compound of gold which has been described, and in type of composition does not correspond to any other ammino-compounds which have been prepared. It should possibly be classed with the compound of ferric chloride and ammonia, $FeCl_3,NH_3$, described by H. Rose (*Ann. Phys. Chem.*, 1832, **24**, 302).

The investigation of these substances and of the alkyl compounds of the other metals of groups I to VIII of the periodic classification is being continued; in view, however, of the poor character of the yields of product obtained, the work necessarily proceeds but slowly.

We desire to express our thanks to Mr. George Matthey, F.R.S., for generously allowing us the use of the large amounts of gold which have been required in the work.

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CCIII.—*Methyl Ethers of some Hydroxyanthraquinones.*

By ARTHUR GEORGE PERKIN.

THE results of an examination of Chay root (*Oldenlandia umbellata*, an Indian dyestuff) made several years ago (Perkin and Hummel, Trans., 1893, **64**, 1160, and 1895, **68**, 817) indicated that this contained, in addition to alizarin and its glucoside, ruberythric acid, numerous other non-tinctorial substances. The most interesting of the latter consisted of dimethyl ethers of anthragallol, the *a*-methyl ether of alizarin, the monomethyl ether of hystazarin, and *m*-hydroxyanthraquinone, and these compounds were present in the sample of root examined, partly in the form of glucosides and partly in the free state.

Somewhat recently Böck (*Monatsh.*, 1902, **23**, 1008) studied the methylation of anthragallol and obtained a dimethyl ether of this colouring matter, which did not agree in melting point with any of the anthragallol dimethyl ethers found to be present in Chay root. As the result of this single observation, Böck makes the following statement: "Es erscheint mir demnach nicht ausgeschlossen dass den Äthern Perkin's und Hummel's nicht die vermuthete Formel zukommt, dass sie vielleicht hydrierte Derivate sind, . . . weiters glaube ich dass ein wirkliche Trennung den Methyläther des Anthragallol, Alizarins und anderer Oxyanthrachinone wie sie in der Wurzel von *Oldenlandia umbellata* vorkommen, keineswegs so leicht gelingt, wie es nach den Arbeiten Perkin's und Hummel's den Anschein hat."

The statements of Böck were noted at the time, but no steps were taken to reply to these criticisms, for although it was quite possible that an error had arisen in regard to one of the three anthragallol dimethyl ethers described as existing in Chay root, it appeared impossible, on considering the facts given in the paper, that the compounds in question could be otherwise than derivatives of anthraquinone. To attempt a re-examination of the root itself would have been hardly worth while, and the subject would have remained undiscussed, had not some residues remaining from the former work been recently discovered. The separation of the various substances was carried out according to the methods given in the previous work, and they will be here alluded to in the order in which they occur in that paper.

Anthragallol Dimethyl Ether (*A*), m. p. 209.—This compound, as formerly shown, is distinguished by the fact that its ammonium salt can be readily isolated in the crystalline condition, and serves to distinguish it from the anthragallol dimethyl ether (*B*) which under the conditions employed is not precipitated in this manner. A re-examination of the substance corroborated previous statements, and the melting point, 209°, remained unaltered, although numerous attempts at further purification were resorted to. Owing to the fact that the red colour of its alkaline solutions disappears on treatment with zinc dust, but returns on exposure to air, it seemed obvious that, taken in conjunction with the evidence previously given, this compound is a derivative of anthraquinone. On the other hand, should it contain an anthranolic or allied grouping by gentle oxidation with chromic acid, the corresponding hydroxyanthraquinone dimethyl ether would be formed, and such a method was employed for the determination of the constitution of members of this class which are present in the root bark of the *Ventilago madraspatana* (Trans., 1894, **66**, 923). It was found, however, that when the anthragallol dimethyl ether (*A*) was subjected to the action of chromic acid in acetic acid solution, an oxidation of this character did not occur, and it suffered gradual destruction with the formation of phthalic acid as previously noted.

Böck (*loc. cit.*) prepared with some difficulty from anthragallol itself the trimethyl ether of this colouring matter, although from his analytical figures he was unable to pronounce this to be a pure compound. As is well known, the difficulty in dealing with phenolic substances of this class is to methylate the hydroxyl group in the ortho-position relatively to the carbinol group, and this, frequently impossible before the introduction of methyl sulphate, was a fairly sure indication of the presence of such a grouping. In attempting to methylate one or other of the natural anthragallol dimethyl ethers, this difficulty should not necessarily occur, as both compounds might already possess the methoxy-group in the ortho-position. To determine this point as regards the anthragallol dimethyl ether (*A*), it was dissolved in methyl alcohol, the solution gently warmed, and treated with equivalent quantities of methyl-alcoholic potash and methyl sulphate until no red coloration was given by the final addition of the former. The mixture treated with boiling water gave a crystalline, pale yellow precipitate, which was collected and washed with hot dilute alkali, when it melted at 168°. It was practically pure, for after two recrystallisations from alcohol and acetic acid this melting point remained unaltered:

Found, C = 68·77; H = 4·78; CH_3 = 14·83.

$C_{14}H_5O_5(CH_3)_3$ requires C = 68·46; H = 4·70; CH_3 = 15·10 per cent.

It consisted of pale yellow needles sparingly soluble in alcohol, and was evidently *anthragallol trimethyl ether*. The melting point agrees with that given by Böck for his ether, but there was every indication in this case that a pure compound had been obtained. Methylation proceeds so easily that from only a very small quantity of the dimethyl ether sufficient of the fully methylated product could be isolated for purposes of characterisation, and accordingly it appears evident that in the original substance there is present a methoxy-group in the ortho-position relatively to the carbinol group.

As previously stated, the anthragallol dimethyl ether (*A*) gives a crystalline ammonium salt when its hot alcoholic solution is treated with ammonia, and it appeared interesting to observe if, by means of alcoholic potassium acetate (Trans., 1899, **76**, 433), a corresponding potassium compound would be precipitated. Such was found to be the case, a crystalline precipitate separating almost immediately:

Found, K = 11·73.

$C_{16}H_{11}O_5K$ requires K = 12·10 per cent.

It consisted of glistening, violet leaflets, which on exposure to the air of the laboratory suffered somewhat rapid decomposition with production of the free dimethyl ether. This proneness to attack by carbon dioxide is not exhibited by the potassium salts of anthragallol, alizarin, and allied colouring matters. The compound is soluble in water with a crimson colour, and the solution is unaffected when raised to the boiling point, at least for short periods.

Anthragallol dimethyl ether (*B*) in general properties closely resembles the substance (*A*), but is characterised by the fact that its ammonium salt is readily soluble in alcohol. An elaborate series of purifications indicated that the melting point previously given for this compound (225—227°) is slightly too low and should be 230—232°, and the acetyl derivative melts at 176—178° instead of 175°. With chromic acid in acetic acid solution it gave no indication of a reduced anthraquinone nucleus, and, when methylated, was readily transformed into anthragallol trimethyl ether, m. p. 168°. It possesses, therefore, the constitution originally assigned to it. Potassium acetate did not precipitate a potassium salt from a hot alcoholic solution of this compound, a property which again distinguishes it from the anthragallol dimethyl ether (*A*).

Alizarin α-Methyl Ether.—This interesting compound has not as yet been produced synthetically from alizarin, all attempts in this direction having resulted in the formation of the corresponding *m*-methoxy-derivative. The methoxy-group present in this substance is much more readily hydrolysed than is usually the case, for prolonged digestion with boiling baryta water is sufficient for this purpose, a precipitate consisting of barium alizarate thus separating. This property therefore accounts for the difficulty in obtaining either this compound or alizarin dimethyl ether by means of methyl iodide, for in this process a prolonged digestion in the presence of free alkali is necessary. A re-examination of the substance confirmed the melting point, 178—179°, previously given, and it was found that by means of alcoholic potash a sparingly soluble potassium salt can readily be prepared. This compound, which crystallises in garnet-coloured, prismatic needles, has evidently the formula $C_{15}H_9O_4K$, but as it was necessary to reserve the small quantity of the alizarin methyl ether available for more important experiments, it was not further studied. To be certain that the methyl ether contained but one free hydroxyl group, it was acetylated, and the acetyl derivative, which melted at 212°, was analysed by Zeisel's method:

Found $CH_3 = 5{\cdot}05$.

$C_{15}H_9O_4{\cdot}C_2H_3O$ requires $CH_3 = 5{\cdot}06$ per cent.

It was therefore a monoacetyl compound.

As a further proof of the constitution of the methyl ether, it was interesting to study its behaviour on methylation, for containing, as is stated, the ortho-methoxy-group, the production from it of alizarin dimethyl ether should proceed without difficulty. Employing methyl sulphate, such was found to be the case, and on treating the product of the reaction with hot water, pale yellow, glistening needles separated. These consisted of the substance in a practically pure condition, but were recrystallised from a mixture of acetic acid and alcohol:

Found $CH_3 = 11{\cdot}21$.

$C_{14}H_6O_2(O{\cdot}CH_3)_2$ requires $CH_3 = 11{\cdot}19$ per cent.

The substance melted at 210—211°. Alizarin dimethyl ether has been prepared by Graebe (*Ber.*, 1905, **38**, 152), by the oxidation of deoxyalizarin dimethyl ether, $C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CH_2}C_6H_2(O{\cdot}CH_3)_2$, and also by Graebe and Thode (*Annalen*, 1906, **349**, 207), by the direct methylation of alizarin with methyl sulphate. As the melting point given by these authors to their compound is 215°, a small quantity of the dimethyl ether was prepared according to the latter method, and in order to be certain that the alizarin employed was pure, advantage was taken of a sample which in the course of the earlier work had been prepared from Chay root.

Although a considerable quantity of methyl sulphate was employed the main product of the reaction was alizarin *m*-monomethyl ether, and only a trace of the dimethyl ether was obtained. The latter, isolated by Graebe and Thode's method, was purified by crystallisation from alcohol and acetic acid; it melted at 210—211°, and was identical with the product formed by the methylation of the natural monomethyl ether.

Hystazarin monomethyl ether, contained in Chay root, was re-examined, and as a result the melting point, 232°, and general properties assigned to this compound were corroborated. It was readily methylated by methyl sulphate in the manner previously described, and the crystalline product was washed with dilute alkali and recrystallised from alcohol and acetic acid:

Found $C = 71{\cdot}61$; $H = 4{\cdot}74$; $CH_3 = 11{\cdot}13$.

$C_{14}H_6O_2(O{\cdot}CH_3)_2$ requires $C = 71{\cdot}64$; $H = 4{\cdot}48$; $CH_3 = 11{\cdot}19$ per cent.

It consisted of pale yellow, glistening needles, melting at 235—236°, sparingly soluble in alcohol, and was evidently *hystazarin dimethyl ether*. As this compound did not appear to have been previously prepared, hystazarin, obtained by the method of Liebermann and Hohenemser (*Ber.*, 1902, **35**, 1778), was methylated by means of dimethyl sulphate. The reaction proceeded without difficulty, and the product, which melted at 235—236°, was identical with that obtained from the natural monomethyl ether.

The *m*-hydroxyanthraquinone isolated from Chay root was so evidently identical with the artificial compound as to render re-examination unnecessary. It was, however, methylated by means of methyl sulphate, and the product of the reaction crystallised from alcohol and acetic acid:

Found $CH_3 = 6{\cdot}18$.

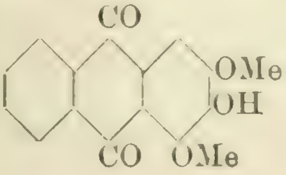
$C_{14}H_7O_2{\cdot}O{\cdot}CH_3$ requires $CH_3 = 6{\cdot}30$ per cent.

This *m*-hydroxyanthraquinone monomethyl ether formed pale yellow needles melting at 192—193°, and was found to be identical with the substance prepared in the same way from synthetical *m*-hydroxyanthraquinone.

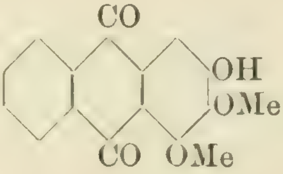
The so-called anthragallol dimethyl ether (*C*), previously described as existing in Chay root, could not, unfortunately, be reinvestigated. The amount previously isolated was very small, approximately 1 gram from 2 cwts. of the root being all that was obtained. If Böck's synthetical anthragallol dimethyl ether (*loc. cit.*), m. p. 159—160°, is a pure substance, then the compound (*C*) for which the melting point 212—213° was given cannot have been a distinct product, but must have been a mixture of the two anthragallol dimethyl ethers (*A*) and (*B*), previously described. In any case this reasoning must be adopted by default, as the matter is not worthy of the enormous trouble which a re-examination of the point would necessitate, and it accordingly can now only be considered as proved that Chay root contains two dimethyl ethers of anthragallol.

The Positions of the Methoxy-groups in the Anthragallol Dimethyl Ethers (A) and (B).

Considering the difficulty with which the α-hydroxyl group present in alizarin and the allied hydroxyanthraquinones is methylated, and, taking into consideration the comparative ease with which the two anthragallol dimethyl ethers of Chay root are converted into anthragallol trimethyl ether, it appeared extremely probable that both compounds contain a methoxy-group in the α-position and would possess one or other of the following formulæ :



(I.)



(II.)

Further, it is reasonable to suppose that Böck's synthetical ether would have the third possible formula and contain a free hydroxyl in the α-position, on account of the difficulty with which the latter group is methylated.

As previously shown, the methoxy-group present in alizarin α-methyl ether somewhat readily suffers hydrolysis in boiling alkaline solutions, and it seemed therefore likely that the corresponding group present in the two anthragallol dimethyl ethers would be hydrolysed at least more readily than those present in the meta-positions relatively to one or other of the carbonyl groups. Should this be the case, anthragallol monomethyl ethers possessing respectively the constitutions (OH : OH : OMe = 1 : 2 : 3) and (OH : OMe : OH = 1 : 2 : 3) would be produced, and the identity of each could be ascertained. Thus the former grouping is that of a methoxyalizarin, a compound which should be soluble in alkali with a blue tint, whereas the latter, which represents a methoxypurpuroxanthin, should yield red alkali salts.

To investigate this point a small quantity of the anthragallol dimethyl ether (*A*) was dissolved in 10 per cent. potassium hydroxide solution, and the liquid heated to 160° in a sealed tube for five hours. The product when cold appeared as a deep blue semi-solid, crystalline mass, which, on solution in boiling water and treatment with acid, deposited an orange-red precipitate. This was collected, well-drained, dissolved in boiling alcohol, and cautiously precipitated with hot water, when it separated completely on cooling in a crystalline condition :

Found $CH_3 = 8{\cdot}48$.

$C_{14}H_6O_3(O{\cdot}CH_3)_2$ requires $CH_3 = 10{\cdot}56$ per cent.

From the analysis it is evident that this product, which formed salmon-red needles melting about 195°, was a mixture of a mono- and a di-methyl ether of anthragallol. On the other hand, this result gave the necessary information, for, as the substance was soluble in alkalis with a blue colour, and readily dyed mordanted calico, there could be little doubt that the monomethyl ether present consisted of *methoxyalizarin*.

An experiment carried out with the anthragallol dimethyl ether (*B*) under the same conditions, at 160°, showed that at this temperature practically no hydrolysis of a methoxy-group occurs, for the melting point of the recovered substance was 225°, and its general properties were identical with those of the original compound. Employing, however, a temperature of 180° for five hours, it was evident that some change had now occurred, for, although the alkaline solution was still red and no trace of blue could be detected, on acidification a deep red precipitate separated. After being crystallised by the addition of boiling water to its hot alcoholic solution it commenced to sinter at 190° and melted completely at 212—213°:

Found $CH_3 = 8{\cdot}10$.

$C_{14}H_6O_3(O{\cdot}CH_3)_2$ requires $CH_3 = 10{\cdot}56$ per cent.

This product was evidently a mixture, but the fact that its alkaline solutions possessed a red colour indicated that the monomethyl ether which had been formed was *methoxypurpuroxanthin* (OH : OMe : OH = 1 : 2 : 3). The corresponding ethoxy-derivative has been previously shown (Trans., 1899, **76**, 446) to be produced when monopotassium anthragallol is heated with ethyl iodide at 230°, and the solutions of the alkali salts of this compound are red. These results therefore adduce considerable proof that the formulæ I and II given above represent respectively the anthragallol dimethyl ethers (*A*) and (*B*), but in case, although this was hardly likely, some change other than hydrolysis of the methoxy-group had been caused by the alkali at the temperature employed, the hydrolysis of these compounds by means of sulphuric acid was now studied.

Experiments first carried out with alizarin *a*-methyl ether, and alizarin dimethyl ether in presence of the concentrated acid at 100°, clearly showed that the *o*-methoxy-group is the most readily attacked in this manner. Thus whereas during half-an-hour's digestion the former compound gives alizarin, the latter, although somewhat less readily, gives alizarin *m*-methyl ether, which, after purification, melted at 224—226°.* Finally, anthragallol trimethyl ether, when studied in this respect, gave at first a compound soluble in alkali with a red coloration, due no doubt to the formation of the dimethyl ether (OH : OMe : OMe = 1 : 2 : 3), but on longer heating further hydrolysis occurred with formation of a monomethyl ether soluble in alkalis with a blue colour, and possessing mordant-dyeing properties. The latter compound, which for reasons given above is evidently the monomethyl ether (OH : OH : OMe = 1 : 2 : 3), on prolonged heating with the sulphuric acid at 100°, did not appear to suffer further change, a point of interest in connexion with the constitution of the anthragallol dimethyl ether (*B*).

Action of Sulphuric Acid on the Dimethyl Ether (*A*).—On heating this compound with excess of the acid to 100°, the alkaline solution of the product examined from time to time soon exhibited a violet tint and finally became blue. It was isolated by addition of water to the hot solution, was purified by crystallisation from alcohol and consisted of orange-red needles melting at 231—232°. Evidently this substance, which readily dyed mordanted calico, is the same compound, in a purer condition, as that formed by the action of potassium hydroxide solution on this anthragallol dimethyl ether, and also by digesting anthragallol trimethyl ether with sulphuric acid; and there can be little doubt that it possesses the constitution of a methoxyalizarin. It was noted in one of the former communications (*loc. cit.*) that when the substance is heated with hydrochloric acid at 150° for an hour, a product of this nature, but evidently contaminated with anthragallol, is formed, and Böck (*loc. cit.*), by the action of sulphuric acid on his dimethyl ether, obtained this anthragallol monomethyl ether, m. p. 233—235°, apparently in a pure condition. As shown above, this methoxyalizarin is but slowly, if at all, attacked by continued heating with sulphuric acid at 100°.

Action of Sulphuric Acid on the Dimethyl Ether (*B*).—By the action of the acid on this substance at 100° for half an hour, the product on solution in alkali gave a red coloration which differed but little from that given by the original compound. Even after two hours no perceptible change occurred in this respect. The precipitate formed by the addition of water exhibited a more orange tint, and probably consisted, at least in part, of an anthragallol monomethyl ether, but on continuing the digestion for seven hours the compound thus produced was now soluble in dilute alkali with a green coloration, and after purification consisted of orange-red needles, which readily dyed mordanted calico. The acetyl derivative of this colouring matter was obtained in pale yellow needles melting at 182—183°, and was without doubt identical with acetylanthragallol.

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* It has been previously observed (Trans., 1899, 76, 446) that this melting point does not agree with that given by Schunck and Marchlewski (*loc. cit.*), namely, 228—229°, but as it has now been prepared by the author in the three distinct ways with an identical result, it is necessary to assume that the lower figure is correct.

This result, therefore, considered in conjunction with the previous experiments, shows clearly that in this compound no methoxy-group can be present in the position 3, for it has been found that the anthragallol monomethyl ether, $OH:OH:OMe = 1:2:3$, is fairly stable towards sulphuric acid at 100°, and, moreover, its formation at any stage of the reaction would have been indicated by the deep blue colour of its alkali salts.

Accordingly, therefore, whereas the methoxy-groups in anthragallol dimethyl ether (*A*), m. p. 209°, occupy the positions 1 and 3 (formula I), in the anthragallol dimethyl ether (*B*), m. p. 230—232°, they occur in the position 1 and 2 (formula II). It is interesting to observe that the formation of sparingly soluble potassium salts exhibited by alizarin α-methyl ether, and by anthragallol dimethyl ether (*A*) when alcoholic potassium acetate is employed, is in harmony with the previous work in connexion with anthraquinone colouring matters, from which proof was deduced that the reactive hydroxyl occupies the meta-position relative to the carbonyl group.

As regards Böck's criticism (*loc. cit.*), that he believes that the methyl ethers of anthragallol, &c., present in Chay root, cannot be separated by any means so easily as the work of Perkin and Hummel indicates, comment is almost unnecessary. In the first place, this author does not produce the faintest evidence that he has conducted an examination of Chay root, or even that he has been in possession of this natural dyestuff; again, there is no assertion in the papers of Perkin and Hummel that the separation of the mixed substances was easy or of a simple character. Thus it is stated on page 825 (*loc. cit.*): "The methods employed for the separation of the yellow substances in Chay root, soluble in baryta water, being *somewhat intricate*, the tables on page 825 are appended with a view to explain the course pursued more clearly." Possibly it is in connexion with these tables that Böck's criticism has arisen; if so, it should be said that it was obviously unnecessary at the time to remark that these tables did not represent a scheme of quantitative analysis, for such an idea could not occur to anyone who had read these papers carefully.

Note on the Emodin Methyl Ether contained in the Ventilago Madraspatana.

It has been recently shown by O. A. Oesterle (*Arch. Pharm.*, 1907, 245, 287) that the wood of *Morinda citrifolia* contains a monomethyl ether of a trihydroxymethylanthraquinone melting at 216°, and this substance he considers is very probably identical with the compound of similar constitution, melting at 200°, isolated by Perkin and Hummel from the root bark of *Ventilago madraspatana* (Trans., 1894, **66**, 923). Although it is quite possible in dealing with substances of this nature, and which exist in plants in conjunction with other compounds possessing closely similar properties, that an error of a degree or two in their melting point might occasionally arise, it seemed unlikely in this case that the conjecture of Oesterle was correct. The substance of Perkin and Hummel, which was proved without doubt to be a monomethyl ether of emodin, was produced by the oxidation of two distinct isomeric compounds, $C_{16}H_{14}O_4$, probably anthranol derivatives, with chromic acid, and was also isolated in minute quantity from the root bark of *Polygonum cuspidatum* (Trans., 1895, **68**, 1084). As the author was in possession of a small quantity of this emodin methyl ether, it was crystallised from acetic acid and benzene, and was found to melt at 200—201° (the melting point previously given is 200°). The acetyl derivative, crystallised from alcohol and acetic acid, melted as before at 185—186°, and when this was hydrolysed with alcoholic potash, the regenerated methyl ether melted at 201°. This emodin methyl ether, from *Ventilago madraspatana*, was, therefore, evidently pure, and the surmise of Oesterle is accordingly not correct. There is no evidence that this author has examined *Ventilago madraspatana*, and it is to be deprecated that criticisms of this kind should be submitted to publication without fuller proof. It is not always possible to retain specimens of such rare substances, and had not this been the case in the present instance, considerable trouble would have been occasioned in the preparation of sufficient substance from the root, in order that the minor points discussed above could be answered.

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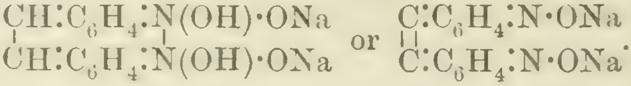
CCIV.—*The Colouring Matters of the Stilbene Group. Part IV. The Action of Caustic Alkalis on para-Nitrotoluene and its Derivatives.*

By Arthur George Green, Arthur Hugh Davies, and Ronald Smith Horsfall.

As the results of investigations conducted by Green in conjunction with former collaborators (*Ber.*, 1897, **30**, 3097; 1898, **31**, 1078; Trans., 1904, **85**, 1424, 1432), the view was advanced that the deeply-coloured (red, violet, or blue), unstable intermediate products which mark the first stage of the action of caustic alkalis on *p*-nitrotoluene and its derivatives are to be regarded as nitrosostilbenes, formed according to the typical scheme:

$$NO_2\cdot C_6H_4\cdot CH_3 + CH_3\cdot C_6H_4\cdot NO_2 \longrightarrow NO\cdot C_6H_4\cdot CH\!:\!CH\cdot C_6H_4\cdot NO.$$

This conclusion was arrived at from a study of the products of oxidation, the compounds themselves being too unstable to admit of isolation. The deep colour of the alkaline solutions of these compounds (when neutral they are pale yellow) was accounted for by assuming for the alkali salts a tautomeric quinonoid form, such as:



$$\begin{array}{l} CH\!:\!C_6H_4\!:\!N(OH)\cdot ONa \\ CH\!:\!C_6H_4\!:\!N(OH)\cdot ONa \end{array} \quad\text{or}\quad \begin{array}{l} C\!:\!C_6H_4\!:\!N\cdot ONa \\ C\!:\!C_6H_4\!:\!N\cdot ONa \end{array}.$$

The reaction appears to be common to *p*-nitrotoluene and all its derivatives, but is greatly facilitated by the presence of electronegative groups in the ortho-position with respect to the methyl group.* This is seen, for example, in the more ready condensation of *p*-nitrotoluenesulphonic acid compared with that of *p*-nitrotoluene itself. At the same time, it is noteworthy that in those cases in which the reaction is greatly accelerated by the presence of a strongly electronegative group, such as $SO_3\cdot C_6H_5$, CN or NO_2, the colour of the intermediate compound is blue instead of red.

In order to investigate the effect of different ortho-substituents, and to obtain further light on the course of the reaction, we have examined the behaviour to caustic alkalis of *p*-nitrotoluene itself, and of its *o*-methyl-, *o*-methoxy-, *o*-cyano-, and *o*-carboxy-derivatives. As in the cases previously investigated, we have endeavoured to characterise the intermediate compounds by oxidation to the stable nitro-compounds by means of air or hypochlorites.

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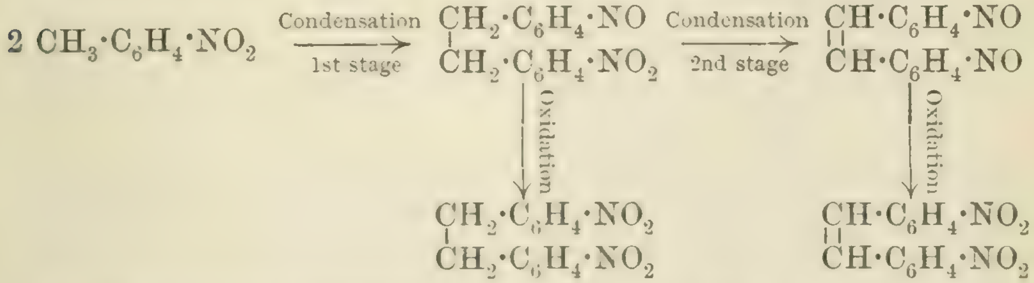
* This fact was first recognised by Green and Stainton. The latter established a close parallelism between the influence of various ortho-substituents on the mobility of the hydrogen atoms of the methyl group when derivatives of *p*-nitrotoluene are submitted to the stilbene condensation, on the one hand, and to Sach's reaction (condensation with nitrosodimethylaniline), on the other. A. G. G.

In the cases examined by Green, Marsden, and Scholefield (the *o*-chloro-derivative and the *o*-phenylsulphonate), only stilbene compounds were obtained on oxidation, and no formation of a dinitrodibenzyl compound was observed, although Green and Wahl had previously obtained from *p*-nitrotoluenesulphonic acid both dinitrodibenzyldisulphonic acid and dinitrostilbenedisulphonic acid, according to the conditions under which the alkaline condensation was performed. We have now found that the ultimate product of oxidation largely depends on the reactivity of the particular derivative. Thus, whilst the *o*-cyano-derivative gave only the corresponding stilbene compound, we obtained from the methyl, methoxyl, and carboxyl derivatives the corresponding dibenzyl compounds; and from *p*-nitrotoluene itself, like its sulphonic acid, either dinitrodibenzyl or dinitrostilbene, according to the conditions employed. It is worthy of note that the derivatives which yield by preference dibenzyl compounds are those which react least easily and give red condensation products, whilst the derivatives which yield chiefly stilbene compounds are those which react most readily and form violet or blue condensation products.

The results point to the conclusion that the alkaline condensation occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage gives rise on oxidation to a dinitrodibenzyl, that of the second stage to a dinitrostilbene. This is shown by the following scheme:



$$\begin{tikzcd}
2\,CH_3{\cdot}C_6H_4{\cdot}NO_2 \arrow[r, "\text{Condensation}", "\text{1st stage}"'] & \begin{matrix}CH_2{\cdot}C_6H_4{\cdot}NO\\ |\\ CH_2{\cdot}C_6H_4{\cdot}NO_2\end{matrix} \arrow[r, "\text{Condensation}", "\text{2nd stage}"'] \arrow[d, "\text{Oxidation}"] & \begin{matrix}CH{\cdot}C_6H_4{\cdot}NO\\ ||\\ CH{\cdot}C_6H_4{\cdot}NO\end{matrix} \arrow[d, "\text{Oxidation}"] \\
 & \begin{matrix}CH_2{\cdot}C_6H_4{\cdot}NO_2\\ |\\ CH_2{\cdot}C_6H_4{\cdot}NO_2\end{matrix} & \begin{matrix}CH{\cdot}C_6H_4{\cdot}NO_2\\ ||\\ CH{\cdot}C_6H_4{\cdot}NO_2\end{matrix}
\end{tikzcd}$$

When oxidation accompanies condensation, as in the experiments described, it would only depend on the speed with which stage one passes into stage two whether the first or the second condensation product was that chiefly attacked by the oxygen. Substituents which increase the reactivity of the substance would therefore favour the formation of stilbene compounds. That this is in fact the case will be shown later.

Relative Influence of Various ortho-Substituents on the Reactivity of the Methyl Group in para-Nitrotoluene Derivatives.

We have endeavoured to obtain an approximate measure of the relative influence exerted by different ortho-substituting groups on the reactivity of the *p*-nitrotoluene complex by observing the relative temperatures at which the colour formation commences under constant conditions of alkalinity and molecular concentration. The experiments were performed as follows: 0·1 gram of *p*-nitrotoluene or the corresponding molecular quantity of one of its derivatives was dissolved in 1 c.c. of pyridine and 5 c.c. of pure methyl alcohol. The solution was contained in a test-tube which could be warmed or cooled as required. Five c.c. of a saturated solution of potassium hydroxide in methyl alcohol (33 per cent. KOH) were added, the mixture was kept well stirred with a thermometer, and the minimum temperature was noted at which colour formation set in. The following results were obtained:

Substance.	Ortho-substituent.	Coloration produced.	Minimum temperature of reaction.
p-Nitrotoluene	H	Crimson	78°
p-Nitro-*o*-xylene	CH_3	,,	79° to 80°
p-Nitro-*o*-tolylmethyl ether ...	$O{\cdot}CH_3$	,,	75° to 77°
p-Nitro-*o*-toluidine	NH_2	,,	81°
p-Nitro-*o*-toluic acid	CO_2H	,,	78° to 79°
o-Chloro-*p*-nitrotoluene	Cl	Violet	23° to 24°
Phenyl *p*-nitrotoluene-*o*-sulphonate	$SO_3{\cdot}C_6H_5$	Blue	about −20°
p-Nitro-*o*-cyanotoluene	CN	,,	,, −20°
2:4-Dinitrotoluene	NO_2	,,	below −20°

The reaction temperatures have, of course, only a relative significance, as they vary greatly with the concentration of alkali employed.

The comparison shows that, whilst the methyl, methoxyl, amino-, and carboxy-groups have but little influence on the reactivity of the compound, the more strongly electronegative groups, sulphophenyl, cyano- and nitro-, exert a powerful effect, that of the nitro-group being greatest. This result is very analogous to the effect on the lability of the chlorine atom in chlorobenzene derivatives exerted by electronegative groups, such as the nitro- and sulphonic acid groups, when occupying an ortho-position.

Action of Caustic Alkalis and Air Oxidation on para-Nitrotoluene.

By acting on *p*-nitrotoluene with alcoholic sodium hydroxide, O. Fischer and Hepp (*Ber.*, 1893, **26**, 2231) obtained small quantities of dinitrodibenzyl and dinitrostilbene. The main product of the reaction was, however, a sparingly soluble, orange-yellow substance, which the above authors term "dinitrosostilbene," but which is probably the dinitroazodistilbene,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot NO_2,$$

formed by further condensation of the true dinitrosostilbene which is first produced. In order to prevent the formation of this condensation product, it is necessary to proceed in such a manner that the intermediate nitroso-compounds are oxidised as soon as they are formed. If, for instance, powdered *p*-nitrotoluene is covered with 33 per cent. alcoholic potash and slightly warmed, the formation of the red nitroso-compound commences at once. The conditions preclude the employment of hypochlorites, but the oxidation of the intermediate compound is readily effected by means of air. To obtain good results and prevent contamination of the product with coloured compounds it is only necessary to take care that the oxidation keeps pace with the colour formation, since the nitroso-compound, if not at once oxidised, quickly undergoes further condensation. Five grams of *p*-nitrotoluene were placed in a wide-necked, conical flask together with 100 c.c. of cold 33 per cent. methyl-alcoholic potash. The red coloration which forms immediately disappears again on vigorous shaking, giving place to a pale yellow, granular precipitate. The operation was continued in the cold with constant shaking until the colour formation only took place slowly and the mixture had become a pale yellow, crystalline magma. This was then filtered by the aid of the pump, the precipitate washed with hot water and hot alcohol, and dried. The product recrystallised from benzene, formed pale yellow needles melting at 180—182°. It was evidently the known 4 : 4′-*dinitrodibenzyl*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$:

Found, N = 10·56, 10·52.

$C_{14}H_{12}O_4N_2$ requires N = 10·29 per cent.

Under the conditions employed above (reaction in the cold), dinitrodibenzyl appears to be almost the sole product. If, however, the temperature of the mixture is slowly raised and the operation continued for a longer period, until finally the colour formation has practically ceased, the product is of a deeper yellow than before and then consists chiefly of a compound which, after alternate crystallisation from nitrobenzene and from glacial acetic acid, was obtained in bright yellow leaflets or flat needles, melting at 292—294°. It proved to be 4 : 4′-*dinitrostilbene*, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, and probably represents this substance in a somewhat purer state than previously obtained. Fischer and Hepp assign to dinitrostilbene the melting point 272°, whilst Walden and Kernbaum (*Ber.*, 1890, **23**, 1958) give 280—285° as the melting point of their higher melting isomeride. We have obtained no evidence of the formation by our reaction of a second isomeride. Analysis gave the following results:

Found, C = 61·95; H = 3·57; N = 10·65, 10·55.

$C_{14}H_{10}O_4N_2$ requires C = 62·2; H = 3·7; N = 10·37 per cent.

The yield of the crude product is nearly theoretical.

In order to distinguish with certainty between stilbene and dibenzyl derivatives in the above and other cases described in this paper, we have made use of the following test, which depends on the more ready oxidation of the ethylene group. A small quantity of the substance is dissolved in a little pyridine, and to the cold solution is added two or three drops of an acetone solution of calcium permanganate. With stilbene compounds, the solution is at once decolorised, whilst with dibenzyl compounds the pink colour persists for several minutes even if gently warmed.

Action of Caustic Alkalis and Air on p-*Nitro*-o-*xylene.*

The operation was carried out in the cold in the same manner as described above. In this case, also, the crude yield was almost theoretical. The product, after recrystallisation from glacial acetic acid, formed lemon-yellow needles, melting at 222—224°. It is not oxidised by permanganate under the conditions described above, and is without doubt 4:4′-*dinitro*-2:2′-*dimethyldibenzyl* (4:4-′*dinitro*-s-*di*-o-*tolylethane*), $NO_2\cdot C_6H_3Me\cdot CH_2\cdot CH_2\cdot C_6H_3Me\cdot NO_2$.

The substance is somewhat sparingly soluble in most solvents. It gave the following results on analysis:

Found, C = 64·14; H = 5·55; N = 9·58, 9·54.

$C_{16}H_{16}O_4N_2$ requires C = 64·0; H = 5·33; N = 9·33 per cent.

Under the conditions of the experiment, the corresponding stilbene derivative was not obtained.*

Action of Caustic Alkalis and Air on p-*Nitro*-o-*tolyl Methyl Ether.*

The *p*-nitro-*o*-tolyl methyl ether employed was obtained by methylation of nitro-*o*-cresol prepared by decomposition of the diazo-compound of *p*-nitro-*o*-toluidine and purification in the manner described by Witt, Noelting, and Grandmougin (*Ber.*, 1890, 23, 3636). After recrystallisation from alcohol, the ether melted at about 72°.

The condensation and oxidation were effected in the same manner as before. The yield of the crude product, insoluble in alcohol, was nearly theoretical, namely, 4·9 grams from 5 grams of tolyl ether taken. The substance was crystallised two or three times from ethyl acetate, and then formed lemon-yellow leaflets melting at 178—180°. It proved to be 4 : 4′-*dinitro*-2 : 2′-*dimethoxydibenzyl* (4 : 4′-*dinitro*-2 : 2′-*dimethoxy*-s-*diphenylethane*),

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* The dinitrodimethylstilbene and dinitrodimethoxystilbene have been since obtained and are at present undergoing investigation. A. G. G.

$$NO_2\cdot C_6H_3(OMe)\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)\cdot NO_2.$$

Analysis gave the following results :

Found, C = 58·43 ; H = 4·80 ; N = 8·72.

$C_{16}H_{16}O_6N_2$ requires C = 57·83 ; H = 4·81 ; N = 8·43 per cent.

A methoxyl determination by Zeisel's method gave :

Found, CH_3 = 8·78.

$C_{16}H_{16}O_6N_2$ requires CH_3 = 9·03 per cent.

The substance is not oxidised by permanganate under the conditions prescribed above.

Under the conditions employed, there was no formation of the corresponding stilbene derivative.*

Action of Caustic Alkalis and Hypochlorites on p-*Nitro*-o-*toluic Acid.*

The *p*-nitro-*o*-toluic acid employed was obtained by saponification of the nitrile (see later) by boiling it for two or three hours with sulphuric acid diluted with half its volume of water. After recrystallisation from dilute alcohol, it formed long, colourless needles which melted at about 178°. When heated with aqueous sodium hydroxide, it gives a deep violet-red coloration, which is converted into a yellow stilbene dyestuff on longer heating. This colouring matter dyes unmordanted cotton direct in bright yellow shades, and is similar to Direct Yellow. The behaviour of the carboxylic acid is therefore quite analogous to that of the corresponding sulphonic acid.

In order to oxidise the violet-red intermediate compound, we have proceeded in a similar manner to that employed for the sulphonic acid by Green and Wahl. Five grams of *p*-nitrotoluic acid were dissolved in 12 c.c. of water by means of 1·4 grams of sodium carbonate. To the hot solution were added 35 c.c. of sodium hypochlorite solution (7·4 per cent. active chlorine), followed immediately by 50 c.c. of sodium hydroxide (33 per cent. NaOH). The mixture was then rapidly heated to the boiling point, when the reaction sets in vigorously and the liquid boils spontaneously for about half a minute. Directly the reaction slackens and the mixture becomes pasty, but before any coloration appears, and whilst there is still a small excess of hypochlorite left (that is, in about one minute from the commencement of the reaction), the whole contents of the flask must be poured quickly into an excess of dilute hydrochloric acid (100 c.c. of concentrated hydrochloric acid and 300 c.c. of water) contained in a large beaker. The operation is somewhat difficult to carry out, as, if the reaction is allowed to proceed a few seconds too long until the hypochlorite is exhausted, colour formation sets in, and the product cannot be subsequently purified. When the operation is correctly conducted, the product is obtained as a pale yellow precipitate, sparingly soluble in water or alcohol. It was purified by several extractions with boiling dilute alcohol (30 per cent.), dried, and recrystallised from cresol. The product separated in colourless plates, which melted with decomposition at 299—300°. Its analysis and properties indicate that it is 4 : 4′-*dinitrodibenzyl*-2 : 2′-*dicarboxylic acid* (4 : 4′-*dinitro*-s-*diphenylethane*-2 : 2′-*dicarboxylic acid*),

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* *Ibid.*

$$NO_2\cdot C_6H_3(CO_2H)\cdot CH_2\cdot CH_2\cdot C_6H_3(CO_2H)\cdot NO_2:$$

Found, C = 53·4, 52·9, 53·5 ; H = 3·51, 3·28, 3·38 ; N = 8·07, 7·83.

$C_{16}H_{12}O_8N_2$ requires C = 53·33 ; H = 3·33 ; N = 7·77 per cent.

It is not oxidised by permanganate in cold pyridine solution or in cold dilute aqueous solution.

We have not yet obtained the corresponding stilbene derivative in a pure state, although in several of our experiments, in which rather different conditions from the above were employed, a product was obtained which gave the reactions of a stilbene compound. The melting point of this substance was about 270°. It is reduced to a crimson-red compound on adding phenylhydrazine or dextrose to the aqueous solution rendered alkaline with sodium hydroxide.

Action of Caustic Alkalis and Air on p-*Nitro*-o-*cyanotoluene.*

The nitrile was prepared from *p*-nitro-*o*-toluidine by Sandmeyer's reaction, and purified by recrystallisation from alcohol. It formed pale yellow needles which melted at 103°. On adding alcoholic potash or strong aqueous potassium or sodium hydroxides to a cold alcoholic solution of the nitrile, excluding air by a current of hydrogen, a brilliant deep blue coloration is produced. This coloration after some minutes slowly changes to violet, and, if air is admitted, it quickly becomes brown, and a dark tarry precipitate is deposited. The blue compound therefore, like other members of its class, is extremely unstable. Since its isolation was impossible, it was at once submitted to oxidation. Both air and sodium hypochlorite were employed as oxidising agents, the product in each case being the same. The hypochlorite, however, gave the best results. Ten grams of the nitrile were dissolved in 30 c.c. of warm pyridine and mixed with 300 c.c. of alcohol. To the cold solution were added 160 c.c. of sodium hypochlorite (4·75 per cent. active chlorine), followed immediately by 60 c.c. of strong aqueous sodium hydroxide. The mixture became warm, and a precipitate separated. This was immediately collected by the aid of the pump, and washed with boiling alcohol. The crude product was a pale yellow, granular precipitate, which melted above 200°. For purification, it was recrystallised several times from nitrobenzene and glacial acetic acid. It proved to be 4 : 4′-*dinitro*-2 : 2′-*dicyanostilbene*,

$$NO_2\cdot C_6H_3(CN)\cdot CH{:}CH\cdot C_6H_3(CN)\cdot NO_2.$$

The compound is sparingly soluble in nitrobenzene, chloroform, or glacial acetic acid, moderately so in pyridine, and almost insoluble in alcohol. It crystallises from glacial acetic acid in small, indistinct, yellow crystals, which melt with decomposition at about 258°. Analysis gave the following results :

Found, C = 60·9, 60·0, 60·2 ; H = 2·75, 2·5, 2·39 ; N = 17·50, 17·87.

$C_{16}H_8O_4N_4$ requires C = 59·9 ; H = 2·52 ; N = 17·54 per cent.

The substance at once decolorises permanganate in a cold pyridine solution. On reduction in cold alcoholic solution by addition of sodium hydroxide and a drop of phenylhydrazine, it is reconverted into the deep blue nitrosostilbene from which it is derived.

We have not been able to isolate a second isomeride. Attempts to convert the nitrile into the carboxylic acid were also unsuccessful, owing to the occurrence of by-reactions on heating with mineral acids.

We desire to express our thanks for a grant from the Chemical Society Research Fund, by which a portion of the expense of this Research has been defrayed.

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CCV.—*The Replacement of Alkyl Radicles by Methyl in Substituted Ammonium Compounds.*

By Humphrey Owen Jones and John Robertshaw Hill.

It was shown by one of us (Proc., 1901, **17**, 205) that dibenzylaniline and quaternary ammonium compounds containing the methyl and benzyl groups, when heated with methyl iodide, yielded benzyl iodide and phenyltrimethylammonium iodide. No other alkyl iodide among those tried, namely, ethyl, propyl, *iso*butyl, and allyl iodides, was found to effect this displacement of the methyl group, and it could not be shown that other groups were displaced by methyl (at this time allyl compounds were not examined). Later (Trans., 1905, **87**, 1726), it was found that the allyl group is displaced from benzylallylaniline by methyl iodide in the cold, and the benzyl group on heating.

At this time, it seemed that the allyl and benzyl groups were the only ones that could be replaced by the methyl group, since optically active compounds containing these radicles racemised readily in chloroform solution, and also their iodides have the greatest capacity for uniting with aromatic tertiary amines, the conclusion that the displacement was dependent on their common properties was apparently justified.

This displacement of benzyl and allyl groups by methyl was found to be general, as proved by the following transformations, in addition to those already mentioned, which were found to take place rapidly when the first-mentioned compound was heated to 100° with methyl iodide alone or with methyl iodide and alcohol or chloroform.

Phenylbenzylmethyl*iso*amylammonium iodide ⟶ phenyldimethyl*iso*amylammonium iodide, phenylbenzylmethyl*iso*propylammonium iodide ⟶ phenyldimethyl*iso*propylammonium iodide, phenyldimethylallylammonium iodide ⟶ phenyltrimethylammonium iodide, phenylmethyldiallylammonium iodide ⟶ phenyltrimethylammonium iodide, phenylmethyl*iso*amylallylammonium iodide ⟶ phenyldimethyl*iso*amylammonium iodide.

Ethyl, propyl, *iso*butyl, and *iso*amyl iodides, when heated with benzyl and allyl compounds, did not effect any displacement, although the odour of allyl or benzyl iodide was always noticeable.

In 1906, some anomalous results were obtained while attempting to prepare a series of compounds containing the phenyl, methyl, and ethyl groups together with propyl, *iso*propyl, *iso*butyl, and *iso*amyl groups. Ethyl*iso*amylaniline and methyl iodide were found to combine slowly in the cold, and the resulting product was, as expected, phenylmethylethyl*iso*amylammonium iodide.

Ethyl*iso*propylaniline and methyl iodide reacted very slowly in the cold, but eventually deposited a crystalline solid which, after repeated crystallisations, melted at 167—168°. It was found to be identical with phenyldimethyl*iso*propylammonium iodide (m. p. 168°), prepared from methyl*iso*propylaniline and methyl iodide. It was evident therefore that the ethyl group was in this case displaced by methyl in the cold.

Ethylpropylaniline and methyl iodide reacted slowly, depositing a gum which became crystalline on standing; after recrystallising, the following numbers were obtained on analysis:

Found, $C = 45{\cdot}12$, $45{\cdot}4$; $H = 6{\cdot}39$, $6{\cdot}4$.

$MeEtPh(C_3H_7)NI$ requires $C = 47{\cdot}2$; $H = 6{\cdot}56$ per cent.
$Me_2Ph(C_3H_7)NI$ „ $C = 45{\cdot}12$; $H = 6{\cdot}14$ „

A similar displacement of the ethyl group has evidently taken place here. This compound and the product from methylpropylaniline and methyl iodide are very soluble, and difficult to recrystallise and purify; hence their absolute identity has not yet been established.

Later, it was found that the series of substituted *p*-bromoanilines already described (Hill, *Proc. Camb. Phil. Soc.*, 1907, **14**, 166) all reacted at 100° with methyl iodide and gave *p*-bromophenyltrimethylammonium iodide. This compound is very easy to isolate and identify, even when formed in quite small quantities, on account of its small solubility in alcohol, its characteristic appearance, and melting point of 200°, a melting point which is higher than that of any of the other ammonium iodides derived from this series of amines.

p-Bromomethylethylaniline or *p*-bromophenyldimethylethylammonium iodide and the corresponding propyl, *iso*propyl, *n*-butyl, and *iso*butyl compounds were found to give some *p*-bromophenyltrimethylammonium iodide after heating at 100° for two hours in a sealed tube with excess of methyl iodide; the *iso*butyl compound appeared to be completely transformed, whilst the ethyl, propyl, and *iso*propyl compounds yielded a moderate quantity of the trimethyl compound.

The *iso*amyl compound, however, seemed to react much less readily, and at first it was thought that no action had taken place; but after prolonged heating, the trimethyl compound was detected: *p*-bromophenylbenzylmethyl*iso*amylammonium iodide yielded the trimethyl compound in somewhat larger quantity.

It was clear therefore that the six saturated hydrocarbon radicles mentioned above behaved in the same way as the benzyl and allyl groups, but that they were not always so readily nor so completely displaced by methyl, as the benzyl and allyl groups.

Attention was now directed to the corresponding series of phenyl compounds to determine whether they behaved in the same way as the bromophenyl derivatives. Phenyldimethylethylammonium iodide and the corresponding propyl, *iso*propyl, *iso*butyl, and *iso*amyl compounds were heated with methyl iodide and examined for phenyltrimethylammonium iodide. This compound is easy to identify on account of its slight solubility, which, however, is much greater than that of the corresponding bromo-compound, and its behaviour on heating, when it volatilises at 220°. All the compounds, except the *iso*amyl derivative, were found to give phenyltrimethylammonium iodide, but even after prolonged heating none could be obtained from this.

It was found, however, that phenylbenzylmethyl*iso*amylammonium iodide yielded some phenyltrimethylammonium iodide after heating with a large excess of methyl iodide.

Here, the ease with which a radicle was displaced seemed to diminish with increasing molecular weight, except that the *iso*butyl group appears to be more readily replaced than the propyl; but the ease with which displacement took place in all cases was distinctly less than in the corresponding bromo-compounds. Phenylbenzylmethyl-*l*-amylammonium iodide (Trans., 1905, **87**, 135) was found to give the trimethyl compound with difficulty, like the corresponding *iso*amyl derivative.

It seems probable that the difference between the *iso*amyl and the other groups as regards the ease with which they are replaced is merely one of degree.

The displacement of alkyl radicles by methyl could take place in one of two quite distinct ways: (1) by direct action between methyl iodide and the ammonium iodide, thus:

$$Me_2Ph(C_7H_7)NI + CH_3I = Me_3PhNI + C_7H_7I,$$

or (2) partial dissociation into tertiary amine and an alkyl iodide might occur in the methyl iodide solution; then the methyl iodide being present in great excess would react with the tertiary amine to form an ammonium iodide until equilibrium was established in solution, thus:

$$\begin{aligned} Me_2Ph(C_7H_7)NI &\rightleftarrows Me_2PhN + C_7H_7I \\ Me_2PhN + CH_3I &= Me_3PhNI. \end{aligned}$$

On consideration, the latter view appears the more probable, since we know that the dissociation postulated does occur in chloroform solution and results in gradual racemisation of active ammonium iodides. That this same dissociation also occurs in solution in alkyl iodides was shown by examining solutions of *l*-phenylbenzylmethyl*iso*propylammonium iodide (Thomas and Jones, Trans., 1906, **89**, 289) in methyl iodide and in ethyl iodide. The salt is extremely sparingly soluble in the iodides, but the addition of a few drops of alcohol enabled a solution to be prepared which gave a rotation great enough for the changes to be observed.

In methyl iodide:

Initial rotation, −0·57°; after six hours, −0·32°; after twenty-four hours, −0·14°; after thirty hours, −0·03°; after forty-eight hours, inactive.

In ethyl iodide:

Initial rotation, −0·62; after six hours, −0·40°; after twenty-three hours, −0·12°; after thirty hours, −0·07°; after forty-eight hours, inactive.

Hence this iodide racemises in methyl and in ethyl iodide solution at practically the same rate as in chloroform (compare Trans., 1906, 89, 290). It follows, therefore, that a dissociation into tertiary amine and alkyl iodide must take place in the case of compounds containing other groups besides benzyl and allyl. Unfortunately, up to the present time, no optically active nitrogen compound is known which does not contain either the benzyl or allyl group together with methyl, otherwise this dissociation could be shown by their autoracemisation.

The ease of replacement would then depend on the extent to which this dissociation into alkyl iodide and tertiary amine occurred. It seems probable that the order of the alkyl radicles as regards extent of dissociation would be the same as that for ease of addition. Taking Wedekind's values for the percentage amount of ammonium salt formed from these alkyl iodides and dimethylaniline in fifty-three hours (*Stereochemie des fünfwertigen Stickstoffs*, 1899, 21), namely, methyl, 89; ethyl, 15; *n*-propyl, 28; *iso*propyl, 5; *n*-butyl, 17; *iso*butyl, 1·6; *iso*amyl, 2·5; allyl, 93; benzyl, 83, we see that the ease of replacement, which is determined presumably by the extent of the dissociation, is roughly in the same order as the ease of formation of quaternary salt by the alkyl iodide in question.

There is, however, an apparent exception in the case of the *iso*amyl group, which we find to be the most difficult to displace, more difficult than the *iso*butyl group, yet its iodide appears to combine with dimethylaniline more readily than the latter.

We therefore examined this point further by allowing mixtures of dimethylaniline and equivalent quantities of ethyl iodide, *iso*butyl iodide, and *iso*amyl iodide to remain for one month at the ordinary temperature. The much longer time was allowed in order to avoid such a large percentage error from the solubility of the salt in the mixture of amine and iodide, which, when very small quantities such as Wedekind obtained (0·15—0·8 gram) are concerned, must exert a disturbing influence on the quantitative results. One-twentieth of a gram-molecule of each mixture was taken, and after standing one month the iodide was separated, dried between filter paper, and weighed (the *iso*butyl compound was crystalline), and found to be 23·6 per cent. for ethyl, 2·0 per cent. for *iso*butyl, and 1·3 per cent. for *iso*amyl. Hence it would appear that the *iso*amyl iodide has not, at any rate, a greater reaction velocity than the *iso*butyl.

Methyl iodide comes third in order of rapidity of reaction with dimethylaniline, and it is therefore surprising to find that it is the one that is capable of replacing all the others; the explanation of this is probably to be found in the very small solubility of the methyl compound as compared with the others, which also accounts for the much greater ease with which replacement takes place in the *p*-bromophenyl than in the phenyl series. The solubilities of the substituted ammonium iodides in alcohol at the ordinary temperature, expressed in grams in 100 grams, are as follows:

				p-Bromophenyldimethyl.	
		Solubility.	Melting point.	Solubility.	Melting point.
Phenyldimethyl.	-methyl	1·1	220° (volatilises)	0·12	200°
	-ethyl	45·1	136	1·15	189
	-*iso*propyl	11·8	168	3·30	167
	-*iso*butyl	24·1	155—156	5·69	167—168
	-*iso*amyl	18·4	138	2·38	176
	-benzyl	2·7	165	—	—

It therefore appears that the ease with which a radicle is displaced by methyl is dependent on two factors; first, the amount of dissociation into tertiary amine and alkyl iodide, of which the rate of formation of the salt from alkyl iodide and amine may be regarded as a measure, and secondly, the solubility of the ammonium salt from which the group is to be displaced. The slight solubility of the trimethyl compound enables this to separate from the solution and so to be removed from the sphere of action.

The ready solubility of the *iso*butyl compound of the *p*-bromophenyl series probably accounts for the fact that this group is more readily displaced than all the others.

On the view expressed above, that the extent of the dissociation is determined by the velocity of addition of the alkyl iodide to the tertiary amine, ammonium salts containing the methyl group should dissociate into amine and methyl iodide to quite a considerable extent. That this is actually the case is shown by the following observations: *p*-bromodimethylaniline was allowed to stand with the iodides of the following radicles, ethyl, propyl, *iso*propyl, *iso*butyl, and *iso*amyl. In the cold, the reaction was extremely slow, except in the case of the ethyl compound. The solid deposited in this case was found to consist chiefly of *p*-bromophenyltrimethylammonium iodide. At 100°, the other four alkyl radicles also yielded a considerable quantity of the trimethyl compound.

It would appear that the following scheme is the probable explanation of these results:

$$C_6H_4Br\cdot Me_2N + EtI \rightleftharpoons C_6H_4Br\cdot MeEtNI,$$
$$C_6H_4Br\cdot Me_2EtNI \rightleftharpoons C_6H_4Br\cdot MeEtN + MeI,$$
$$C_6H_4Br\cdot Me_2N + MeI \rightleftharpoons C_6H_4Br\cdot Me_3NI.$$

The quaternary salt first formed is dissociated in two distinct ways, so that in the solution we have an equilibrium between two alkyl iodides and two tertiary amines. The very small solubility of the trimethyl compound then determines the separation of this salt from the solution. A dissociation of ammonium salts into two amines and two alkyl iodides on heating has been observed by Wedekind (*Ber.*, 1902, **35**, 766).

The results may be summarised as follows: the groups, allyl, benzyl, ethyl, *iso*butyl, propyl, *iso*propyl, and *iso*amyl, are displaced from ammonium salts by the methyl group on treating with methyl iodide, sometimes in the cold, more usually on heating. The displacement takes place owing to the salt dissociating in methyl iodide solution into tertiary amines and alkyl iodides; an equilibrium is set up between the dissociated amines, iodides, and the methyl iodide, and, since in each case the trimethyl compound is much less soluble than the other, this separates, and so is found in much greater quantity than the other in the solid product.

The order given is roughly that of the ease of displacement of these radicles, which is determined by the extent of the dissociation and the solubility of the ammonium salt in question. The *iso*amyl group is the most difficult to displace.

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C_{36} Group.
$C_{36}H_{40}O_{14}N_4, H_2O$ 96
$C_{36}H_{30}O_{18}S_6Ce_2, 23H_2O$ .. 477
$C_{36}H_{30}O_{24}S_6Ce_2, 12H_2O$. 476
$C_{36}H_{30}O_{24}S_6Ce_2, 17H_2O$. 476
$C_{36}H_{40}O_8N_2Br_2, H_2O$ 96
$C_{36}H_{51}O_{15}N_6Co$ 901
$C_{36}H_{57}O_3N_6Co$ 900
$C_{36}H_{36}O_{18}N_6S_6Ce_2. 16H_2O$ 477
$C_{36}H_{40}O_8N_2Cl_6Pt$ 97
$C_{36}H_{40}O_8N_2Cl_6Pt, H_2O$ ... 97
$C_{36}H_{44}O_{10}N_2Cl_6Pt, 2H_2O$ 95

C_{37} Group.
$C_{37}H_{43}O_{10}N_5$ 351
$C_{37}H_{44}O_5N_2$ 1980

C_{38} Group.
$C_{38}H_{62}O_4, H_2O$ 1917
$C_{38}H_{26}N_2Cl_8Pt$ 1661
$C_{38}H_{26}O_4N_2Cl_2Cr$ 1662
$C_{38}H_{26}O_7N_2Br_6Cr_2$ 1664, 1665
$C_{38}H_{30}O_{10}Cl_6S_2Pt$ 1121
$C_{38}H_{34}ON_2Cl_6Pt$. 1936, 1937
$C_{38}H_{36}O_2N_2Cl_6Pt$ 1938
$C_{38}H_{26}O_7N_2Cl_2Br_4Cr_2$ .. 1663

C_{39} Group.
$C_{39}H_{64}O_4$ 1918
$C_{39}H_{22}O_{16}N_8$ 1240

C_{40} Group.
$C_{40}H_{26}$ 1108, 1112
$C_{40}H_{25}O_{14}N_7$ 1236, 1237
$C_{40}H_{25}O_{15}N_7$ 1238

PAGE
$C_{40}H_{34}N_2Br_6$ 1243
$C_{40}H_{36}N_2Cl_6Pt$ 1245
$C_{40}H_{36}N_2Cl_6Pt, 2H_2O$ .. 1242

C_{41} Group.
$C_{41}H_{32}O_{11}$ 1777

C_{42} Group.
$C_{42}H_{36}O_{11}N_2Cr_2$ 1622

C_{44} Group.
$C_{44}H_{40}O_8N_2Cr$ 1625
$C_{44}H_{80}O_7N_2S_2Si_2$ 229
$C_{44}H_{80}O_7N_2S_2Si_2, 4H_2O$. 229

C_{48} Group.
$C_{48}H_{58}O_{13}S_2Cr_2$ 527
$C_{48}H_{58}O_6Cl_6S_4Pt$ 527

C_{50} Group.
$C_{50}H_{44}O_{15}N_2Cr_2$ 1623
$C_{50}H_{40}O_2N_4Cl_3Fe$ 903

C_{52} Group.
$C_{52}H_{66}O_{13}S_2Cr_2$ 528
$C_{52}H_{66}O_6Cl_6S_2Pt$ 527

C_{54} Group.
$C_{54}H_{33}O_4N_4Cl_4Au$ 1239
$C_{54}H_{34}O_4N_4Cl_6Pt$ 1239

C_{56} Group.
$C_{56}H_{40}N_2Cl_6Pt$ .. 1236, 1237
$C_{56}H_{40}N_2Cl_6Pt, 2H_2O$ 1235, 1236
$C_{56}H_{40}N_2Cl_6Pt, 3H_2O$ .. 1235
$C_{56}H_{40}O_2N_2Cl_6Pt, 2H_2O$ 1238
$C_{56}H_{40}O_2N_2Cl_6Pt, 3H_2O$ 1238

C_{60} Group.
$C_{60}H_{42}O_{24}S_6Ce_2, 20H_2O$ .. 476
$C_{60}H_{90}O_{24}S_6Ce_2, 20H_2O$ .. 477
$C_{60}H_{48}O_{18}N_6S_6Ce_2, 32H_2O$ 477
$C_{60}H_{52}O_5Cl_6S_5Pt$ 901

C_{70} Group.
$C_{70}H_{52}O_{15}N_2Cr_2$ 1624

C_{72} Group.
$C_{72}H_{84}O_{16}N_{10}$ 351

C_{84} Group.
$C_{84}H_{70}O_8N_4Cl_6Pt$ 1623

C_{88} Group.
$C_{88}H_{78}O_8N_4Cl_6Pt$ 1625

C_{100} Group.
$C_{100}H_{86}O_{16}N_4Cl_6Pt$ 1624

ERRATA.

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Page	Line	
37	5	*for* “$O_2:C_6H_2Br_2:N_2$” *read* “$O:C_6H_2Br_2:N_2$.”
256	13*	,, “$C_{16}H_{12}O_6N$” *read* “$C_{16}H_{19}O_6N$.”
335	6	,, “$C_{10}H_{14}O_2N_2$” *read* “$C_{18}H_{14}O_2N_2$.”
350	7	,, “$C_{35}H_{41}O_5N_5$” *read* “$C_{35}H_{41}O_6N_5$.”
354	2	,, “$\alpha\gamma$” *read* “$\alpha\delta$.”
425	18	,, “5:1-Hydroxy-” *read* “1-Hydroxy-.”
548	6*	,, “$C_2H_{10}O_2$” *read* “$C_9H_{10}O_2$.”
763		*transpose* Fig. 3 to page 767.
767		,, Fig. 2 ,, 763.
920	15*	*for* “$\alpha\alpha$-carboxyphenylphenylthiocarbonate” *read* “$\alpha\alpha$-carboxyphenylphenylthiocarbamide.”
1375	2*	,, “t” read “t_2.”
1376	2* and 11*	in equation, *for* “t_1, t_2, and t_3” read “z_1, z_2, and z_3” respectively.
1377		in equation (19), in right-hand expression, *for* “ = ” *read* “ – ,” and in equation (21*a*), in left-hand expression, *for* “k''” read “k_2''.”
1441	2*	*for* “$C_8H_7O_4N$” *read* “$C_8H_{11}O_4N$.”
1531	18	,, “B” *read* “β.”
1591	2	,, “7(10)-*amino*-1-*naphthacenequinone*” read “7(10)-*amino*-1-*hydroxynaphthacenequinone*.”
1640	4*	,, “$C_{16}H_{12}O_4$” *read* “$C_{12}H_{12}O_4$.”
1662	4*	,, “$C_{13}H_{19}NClBr_2$” *read* “$C_{19}H_{12}NClBr_2$.”
1749	2*	,, “mostly” *read* “only.”
1750	6	,, “Serturnier” *read* “Sertuerner.”
1750	7	,, “ten years” *read* “decades.”
1752	17*	,, “biose” *read* “glycollaldehyde.”
1752	16*	,, “Mackenzie” *read* “A. McKenzie.”
1755	7	,, “no less than” *read* “some.”
1755	10	,, “as well as” *read* “of.”
1756	2	*delete* the sentence “I may mention . . . . the yeast cell.” Note.—Buchner has recently informed me that his earlier statement (*Oesterreich. Chem. Zeit.*, 1898, No. 7), from which the above conclusion could be drawn, was meant in a different sense.—E. F.
1760	6	*for* “H. Kossel” *read* “A. Kossel and H. D. Dakin.”
1761	26	*after* “acid” *insert* “ornithine, oxyproline, and *iso*leucine.”
1763	15	*for* “ten years” *read* “decades.”
1764	6*	,, “ten years” *read* “decades.”
1765	2	,, “blood” *read* “flower.”
2034	20 & 21	,, “$3Hg_2O\cdot N_2O_5$” *read* “$3Hg_2O,N_2O_5$.”
2034	26	,, “$HgO\cdot 2Hg_2O\cdot N_2O_5$” *read* “$HgO,2Hg_2O,N_2O_5$.”
2035	9, 10 & 21	*for* “$Hg'\cdot Ag$” *read* “Hg',Ag.”
2036	2, 4, 6, 9, 21, 22 & 24	,, “$Hg'\cdot Ag$” *read* “Hg',Ag.”

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* From bottom.

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